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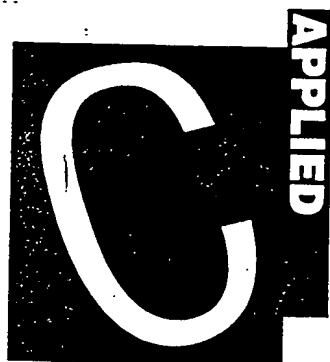
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Review

Aniline alkylation over solid acid catalysts

Sankarasubbier Narayanan*, Kiranmayi Deshpande

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India



Editors

Prof. H.H. Kung
Department of Chemical Engineering
Northwestern University
Room E136, 2145 Sheridan Road
Evanston, IL 60208-3120
USA
Fax: (+1-847) 4671018
E-mail: hkung@nwu.edu

Prof. K. Segawa
Sophia University
Dept. of Chemistry
7-1 Kioi-cho, Chiyoda-ku
Tokyo 102-8554
Japan
Fax: (+81-3) 32384350
E-mail: k-segawa@sophia.ac.jp

Prof. J.C. Vedrine
Leverhulme Centre for Innovative Catalysis
Department of Chemistry
The University of Liverpool
PO Box 147
Liverpool L69 7ZD
UK
Fax: (+44-151) 7943589
E-mail: vedrine@liverpool.ac.uk

Associate Editor:

Prof. L. Guczi
Dept. of Surface Chemistry and Catalysis,
Institute of Isotope and Surface Chemistry,
Hungarian Academy of Sciences,
P.O. Box 77, Budapest, H-1525 Hungary
Fax: (+36-1) 3959001; E-mail: gucci@alpha0.iki.kfki.hu

News Brief Editors:

Prof. G.J. Hutchings
Cardiff University, Wales, UK
Department of Chemistry
P.O. Box 912, Cardiff CF10 3TB
UK
Fax: (+44-1222) 874075
E-mail: hutch@cf.ac.uk

Prof. B.H. Davis
University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, KY 40511-8433
USA
Fax: (+1-606) 2570302
E-mail: davis@caer.uky.edu

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Review

Aniline alkylation over solid acid catalysts

Sankarasubbier Narayanan*, Kiranmayi Deshpande

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

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Abstract

Alkyl anilines are useful intermediates. *N*-ethylaniline is an important dyestuff. *N,N'*-diethylaniline is used as a co-catalyst in polymerization reactions. It is also used as an inhibitor of acid corrosion in metallic vessels and as an antioxidant for lubricating oils. 2,6-diethylaniline is an important intermediate in the synthesis of weedicide, butachlor. Vapor phase aniline alkylation over several solid acid catalysts such as oxides, clays and zeolites and on their modified forms are discussed in detail. From the enormous information collected on the physico-chemical characteristics of the various solid acid catalysts and from the aniline activity studies, it has been observed that the structural features of the catalysts do play an important role in controlling conversion and selectivity. A reasonable acidity and activity relationship is established. A mechanism for aniline alkylation, with alcohol as alkylating agent, involving both the Brønsted and Lewis acid sites has been proposed. This review is based mainly on the work carried out in our laboratories as a part of envirocatalysis involving alkylation reactions over solid acids. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Solid acid catalysts; Oxides; Clays; Zeolites; Modification by oxide impregnation; Solid state ion-exchange; Ion-exchange; Acid activation and pillaring; Aniline alkylation; Activity; Selectivity and mechanism

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* Corresponding author. Tel.: +91-40-715-33-74;
fax: +91-40-717-37-57; +91-40-717-33-87.
E-mail address: snarayanan@iict.ap.nic.in (S. Narayanan)

Friedel–Crafts catalysis is one of the major and industrially important processes used widely in the synthesis of low and high volume chemicals. Acylations, benzoylations, alkylations and sulphonylations giving a wide range of useful products like ketones, alcohols, alkyl aromatics and sulphones are included in

this name reaction. Petrochemical industry is also a beneficiary of this class of reaction where a number of alkyl hydrocarbons are synthesized by alkylation reactions. The conventional catalysts used in these reactions are AlCl_3 , HF, H_2SO_4 , BF_3 and the likes. Most of the batch processes use AlCl_3 as soluble acid catalyst which is inexpensive, very reactive and is one of the most powerful Lewis acids. Unfortunately, it is difficult to handle AlCl_3 and similar metal halides as catalysts since they get readily hydrolyzed. Very often such catalysts are required in stoichiometric quantities. A large inventory of these materials pose health, safety and storage problems. Furthermore, the traditional route of liquid phase alkylation using mineral acids and AlCl_3 as catalysts suffer from the disadvantages of high capital cost, reactor corrosion, formation of by-products and the difficulty in catalyst regeneration. In recent times, the scientists world wide have been devoting their attention to the development of environmentally friendly catalysts for the production of industrially important chemicals and chemical intermediates.

The use of safe solid acids in place of traditional Friedel-Crafts catalysts and mineral acids has become important. Several alkylation reactions of aromatic hydrocarbons and functional aromatic hydrocarbons have been tried out over zeolites, oxides, mixed oxides and supported oxides. Clays such as montmorillonite having acidic functions are also being considered as alternate catalysts for these reactions. Clays have also been modified for this purpose by pillaring with polyhydroxy metal cations such as Zr, Al, Cr, Ga etc., acid activation, ion exchange with transition metals and by metal oxide impregnation.

We have been pursuing the synthesis of chemicals and chemical intermediates by several catalytic routes and the Friedel-Crafts alkylation is one of them; for

example, the alkylation of hydrocarbons as well as functional aromatics and hetero-aromatics [1]. In this endeavor, solid acid catalysts have been used as alternates to the conventional corrosive Friedel-Crafts catalysts. Alkylation of phenol was studied [2-8] over oxides, supported oxides, mixed oxides and zeolites. Alkylphenols are important chemicals and chemical intermediates, especially in agrochemical and pharmaceutical industries. *o*-Cresol is used in the synthesis of herbicides. Dialkyl phenols such as 2,6-xylenol are used in the manufacture of industrial grade plastics polyphenylene oxide (PPO) and paint. 2,3,6-trimethylphenol, starting material for synthetic vitamin E can be prepared selectively (80-90%) and 95-100% *m*-cresol conversion at 773 K and 20-30 bar [5].

Aniline alkylation, another important chemical reaction, has been studied in great detail. *N*-ethylaniline is an important dyestuff. *N,N'*-diethylaniline is used as a cocatalyst in polymerization reaction and as an inhibitor of acid corrosion in metallic vessels as well as an antioxidant for lubricating oils. 2,6-diethylaniline is an important intermediate in the synthesis of weedicide, butachlor. Bhattacharya and Nandi [9] have reported the liquid phase synthesis of *N,N'*-diethylaniline at 500 psi using mineral acids as catalysts and the results are given in Table 1. Under the experimental conditions, HCl and H_2SO_4 are more active than HBr, HI and H_3PO_4 for the dialkylation of aniline. Vapor pressure of 660 psi is found to be the optimum for the reaction. Prolonging residence period beyond 2 h not only decreased conversion of aniline but also has resulted in the increased formation of undesirable tarry material. With the increasing awareness of environmental issues, various solid acid catalysts have been tried for this reaction. These include oxides [10-15], multimetal

Table 1
Liquid phase aniline ethylation using mineral acid catalysts^a [9]

Catalyst	Volume of catalyst (cm^3)	Mole ratio of aniline:ethanol	% Unreacted aniline	% Conversion	
				Diethylaniline	Ethylaniline
HCl	4.5	1:0.15	14.23	24.79	60.48
HBr	8.5	1:0.16	20.75	19.45	58.76
HI	9.0	1:0.15	25.10	18.76	55.22
H_2SO_4	1.5	1:0.08	40.14	20.57	38.15
H_3PO_4	1.0	1:0.053	70.15	6.52	22.30

^a Reaction temperature=498 K, Pressure=500 psi, Residence period=1 h.

Table 2
Aniline methylation with dimethyl carbonate as the alkylating agent^a

Catalyst	Temperature (K)	W/F (g h mol ⁻¹)	% Aniline conversion	% Selectivity <i>N</i> -methylaniline
^b Al ₂ O ₃	523	12.1	22	93
^b MgO	523	12.1	1	100
^b NaY (5.6)	453	2.08	82	88
^b HY (5.6)	453	2.08	4.1	98
^b NaX (2)	453	2.08	94	92
^b Na Mordenite (10.2)	473	6.1	1.7	100
^b Na ZSM-5 (43.5)	453	2.08	10.4	99
^b H-ZSM-5	473	6.1	2.1	95
^c K-β (13.7)	408	0.206	63	93
^c K-Y	408	0.206	78	92
^c K-X	408	0.206	86	82
^c K-EMT (3.9)	408	0.206	81	92

^a DMC:Aniline=1.24:1; N₂/DMC+aniline=1. Value in brackets indicates SiO₂/Al₂O₃ ratio.

^b [37].

^c [38].

catalysts [16], Raney–Nickel [17], zeolites [18–26], AEL type molecular sieves [27,28] and clays [29–35]. The various alkylating reagents used include olefins [36], alcohols [12–15,18–23,29–35] and dimethyl carbonates [37–39]. The reaction using dimethyl carbonate as the alkylating agent is interesting with high selectivity to *N*-methyl aniline (Table 2) especially over zeolites even at a low temperature of 408 K.

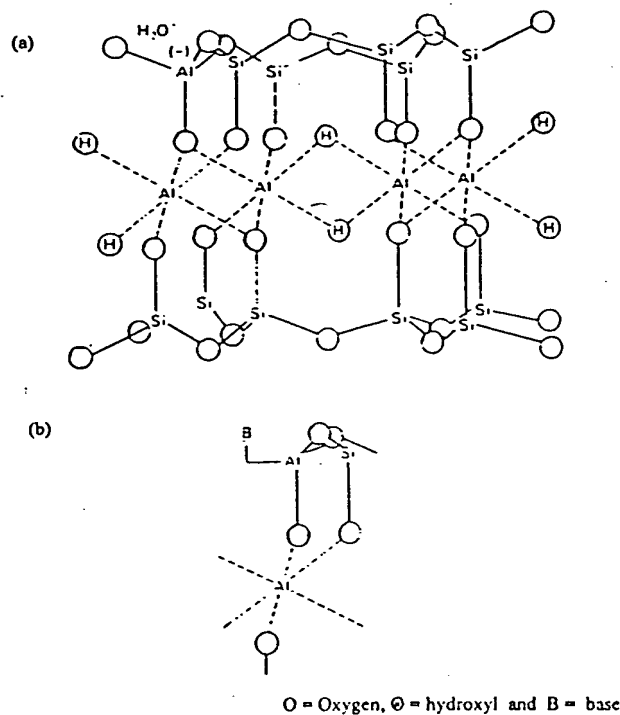
1.1. Clays

The use of clays as catalysts is well known. They are used extensively in petroleum industry for isomerization and cracking reactions. One of the problems of using clays as catalysts, is that they deactivate at high temperatures due to structural collapse. The introduction of silica alumina and synthetic zeolites might have slightly over shadowed the significance of clays in petroleum refining. Nevertheless, clays retain their continuing importance as they constitute the matrix of many industrial catalysts based on zeolites. They have also found favorable application in reactions which do not require drastic temperature conditions, for example, etherification [40], isomerization [41], alkylation reactions [29–35,42].

Clays are silicate minerals of aluminium and magnesium hydroxide. They contain continuous two-dimensional tetrahedral sheets of composition T₂O₅ (T-tetrahedral, normally Si⁴⁺, Al³⁺ or Fe³⁺) in which individual tetrahedra are linked with adjacent

tetrahedron by sharing three corners comprising the basal oxygens to form a hexagonal mesh pattern. The fourth tetrahedral corner, i.e., the apical oxygen points in a direction normal to the sheet and at the same time forms a part of an immediately adjacent octahedral sheet in which individual octahedra are linked laterally by sharing octahedral edges. The common plane of junction between the tetrahedral and the octahedral sheets consists of the shared apical oxygens plus the unshared –OH groups that lie at the center of each tetrahedral six-fold ring at the same *z* level as the apical oxygens. The octahedral cations are normally Al³⁺, Mg²⁺, Fe²⁺ and Fe³⁺, but other medium size cations of Li⁺, V⁵⁺, Ti⁴⁺, Cr³⁺, Mn⁴⁺, Co³⁺, Ni²⁺, Cu²⁺ etc. also occur in some species.

Montmorillonite, the most commonly occurring smectite is a 2:1 dioctahedral clay. The tetrahedral layer has Si⁴⁺ linked to the adjacent Si⁴⁺ and to the Al³⁺ or Mg²⁺ of the octahedral layer by oxygens and hydroxyl groups. The negative charge on the layers is mainly due to the substitution of octahedral Al³⁺ by Mg²⁺. Al³⁺ in aluminosilicates is the source of the acidic nature of the surface [43]. Al³⁺ proxying for Si⁴⁺ in tetrahedral coordination in an aluminosilicate gives rise to a net negative charge. A charge balancing H₃O⁺ associated with such tetrahedral Al³⁺ corresponds to a Brønsted acid site. An Al³⁺ in a three-fold coordination, perhaps occurring at an edge or arising from a Si–O–Al bond rupture and dehydroxylation of the Brønsted site would lead to the Lewis site [44].



(a) An off axis projection of a 2:1 dioctahedral clay mineral with a Brønsted acid site
 (b) A possible configuration for a Lewis acid site

Fig. 1. Acid sites in clay layers.

The presence of Brønsted and Lewis acid sites in clay layers are shown in Fig. 1. Various modifications such as, acid activation and pillaring, alter the structure of clay and thereby affect the acidity.

Naturally occurring clays may not be efficient catalysts for acid catalyzed reactions, especially if the unit cell composition is neutral and is balanced with alkali or alkaline earth cations. However, the surface hydroxyl groups of the clays can still contribute to the catalysis. The best way of activating the clay is by acid leaching and by pillaring with polyhydroxy metal cations or metal clusters. Modifications can also be effected by impregnation of metal oxides such as vanadia, chromia, zirconia and alumina. The structure, the composition of the metal oxide and the extent to which they interact with the clay support may all influence the catalytic activity of the parent clay material. Impregnation also modifies the acidity, due to varying dispersion and interaction with

the oxide surface, and contribute to conversion and selectivity.

1.2. Zeolites

Zeolites are another set of solid acids that have been evaluated for their alkylating property. They are crystalline aluminosilicates with three-dimensional open structured frame work which encloses cavities or channels that run through out the structure. The three dimensional network of $[\text{AlO}_4]$ and $[\text{SiO}_4]$ tetrahedra are linked to each other through doubly bridging oxygen atoms. Each Al atom incorporated into the frame-work creates a negative charge. The excess charge is balanced by exchangeable cations. These cations in their hydrated form occupy cages or the channels. ZSM-5 is a medium pore zeolite containing 10 membered ring pore opening. The frame work of ZSM-5 contains a primary pentasil unit arranged in

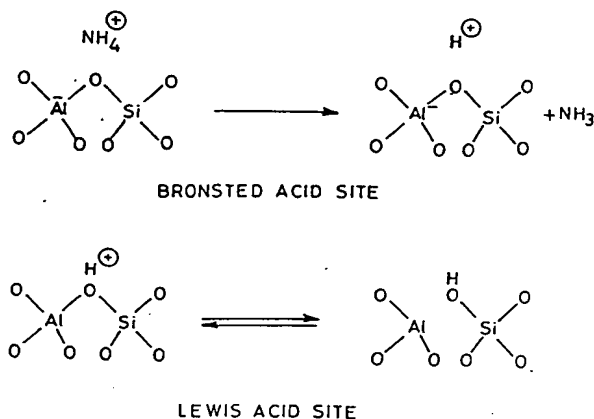


Fig. 2. Acid sites in zeolites.

a novel configuration of tetrahedra linked to form secondary building unit consisting of eight five membered rings. These units join through edges to form chains which extend along z-axis. The chains are connected to form sheets and the sheets are linked across mirror plane forming four and six membered rings leading to three dimensional framework structure of ZSM-5.

The acidity in zeolites arises by the substitution of Si in the framework position by a trivalent metal atom such as Al. When the charge compensating ion is a proton, the zeolite exhibits Brønsted acidity. Lewis acidity arises from the trivalent Al or cationic species like alkali, alkaline earth or other cations (Fig. 2). The treatment of zeolites at high temperature transforms the Brønsted acidity to Lewis acid sites. Acidity increases with the Al content. In hydrogen form, ZSM-5 possesses both the Brønsted and Lewis acid sites. Acidity can be introduced into zeolites in a number of ways: (i) ion exchange with NH_4^+ followed by thermal decomposition; (ii) hydrolysis of ion exchanged polyvalent cation followed by partial dehydration; (iii) reduction of exchanged metal ions to a lower valence state.

The special feature of zeolites is that they can act as molecular sieves, admitting some molecules to the large intracrystalline surface for reaction while excluding others which are too large to enter or preventing production of molecules which are too large to exit. This effect is referred to as shape selectivity which can be reactant shape selectivity, product shape selectivity,

or restricted transition state selectivity. Molecular traffic control proposed by Derouane and Gabelica [45], is another phenomenon which ensures shape selectivity. According to this phenomenon, reactants preferentially enter through a set of channels while product diffuses out through another, preventing occurrence of counter diffusion limitations. Zeolites have been modified by several ways to improve their catalytic and sieving properties. These modifications can be either by direct hydrothermal synthesis or by post-synthesis methods and include isomorphous substitution, cation exchange and metal loading. During the process of zeolite synthesis, as per the requirement of the reaction, the metal ions are isomorphously introduced. The transition metal ions introduced may occupy pores, the external sites, the zeolitic frame work, the exchange sites or the defect sites. Most of the zeolites are synthesized in cationic form in which the positively charged cations balance the negatively charged framework. These extra framework cations can be replaced by other cations. Zeolites have also been used successfully as supports. The combination of acid base and redox properties impart bifunctionality. Several metallic and bimetallic catalysts have been prepared using zeolites as supports [46–56]. Metals are loaded over zeolites by ion exchange, impregnation or adsorption from gas phase. Solid state exchange technique is a recent method employed for incorporating the transition metal ions into the zeolite matrix. These modifications affect the structure of zeolite and thereby influence the catalytic activity.

1.3. Oxides

Oxides are one of the seminal solid catalysts used for the industrial processes involving dehydrogenation, oxidation, ammoxidation, polymerization etc. Due to their acidic function, they have also gained importance as alkylation catalysts. Alumina, silica, transition metal oxides, and silica–alumina in their various modified forms have been evaluated. Even though they have been replaced by catalytic materials like zeolites and mesoporous materials, their use as catalysts still holds promise. In combination with the high surface area, thermally stable materials, they render the catalytic system with the best properties of both the components. The transition metal oxides, possess both Lewis and Brønsted acidity. Lewis acid-

ity arises due to the ability of the metal ion to exist in various oxidation states. Chromia is a well known Lewis solid acid [57]. Brønsted acidity in the bulk oxides is due to the loosely bound protons associated with the oxide ions. V_2O_5 and ZrO_2 contain both Lewis and Brønsted acid sites [57,58]. Very weak Brønsted acidity has been noted on silica [59]. However, impregnation of acidic metal oxide over SiO_2 is found to enhance the acidity of the system [12,60].

2. Alkylation reactions

Alkylation is an electrophilic substitution reaction. The electrophile i.e., the carbonium ion is formed from the alkylating agent viz., olefins, alcohol or alkyl halide with the help of the acid sites on the catalyst surface. The solid acids, because of the presence of both Lewis and Brønsted acid sites, function successfully as alkylation catalysts. Some examples of the alkylation reactions using clays, oxides and zeolites are given in Table 3. Aniline alkylation is an acid catalyzed reaction. Vapor phase aniline alkylation has been studied over zeolites using alcohol [18–26], olefins [36],

and dimethyl carbonate [37–39]. The investigations though have stressed on the influence of acidity over the conversion and selectivity pattern [24–26,66], the type and strength of acid sites most suitable for the reaction is still not clear. We have studied the effect of structural modifications of the catalyst over acidity and hence on the conversion of aniline and selectivity of alkyanilines. We have carried out vapor phase aniline alkylation over oxides, supported oxides especially V_2O_5 impregnated SiO_2 , montmorillonite K10, acid activated Wyoming montmorillonite and alumina pillared montmorillonite. Some of the observations reported by us, on clay catalyzed aniline alkylation, probably form the first reports.

Aniline alkylation has also been studied on ZSM-5 synthesized with and without template ($SiO_2/Al_2O_3=28-150$). The influence of various metal oxides especially vanadia, over zeolites on the acidity and on the conversion and selectivity pattern is studied. Vanadia is wet impregnated over the zeolites. Solid state exchange of vanadium ions into zeolite was also adopted and the resulting catalytic parameters have been related to the catalysis. Preparation methods followed for different catalytic materials

Table 3
Examples of alkylation reactions using oxide, clay and zeolite catalysts

Reactant	Reagent	Catalyst
<i>Alkylation of aromatic hydrocarbons</i>		
(i) With olefins		
Benzene	Ethane	Wyoming montmorillonite expanded with $AlCl_3$ and/or silanized with $(EtO)_4Si$ [61]
Toluene	Ethane	HZSM-5 [62]
(ii) With saturated hydrocarbons		
Benzene	Admantane	$FeCl_3$ doped montmorillonite K10 [61]
(iii) With alcohols		
Benzene, toluene naphthalene	Aliphatic alcohols, cyclopentanol	$ZnCl_2$ clay [61], Al_2O_3 expanded smectite clay [61]
Benzene	Ethanol	HZSM-5 [63]
Toluene	Methanol	Pillared montmorillonite, pillared saponite, HZSM-5, HY [61]
Naphthalene, methyl naphthalene	Methanol	HZSM-5 [64]
(iv) With halides		
Benzene	Benzyl chloride	Transition metal salts impregnated on montmorillonite K10 [65]
<i>Alkylation of phenols</i>		
Phenol	Isobutene	Activated clay [61]
	Oleic acid	Bentonite [61]
	Methanol	Supported/mixed oxides [2–9]
<i>Alkylation of aromatic amines</i>		
Diphenyl amine	Styrene	Bentonite and Triton B [61]

Table 4
Preparation and modification methods for oxide, clay and zeolites

Starting material	Method of modification	Nomenclature used in the study
Silica (Akzo)	Wet impregnation, air dried, calcined at 723 K	
NH ₄ VO ₃ in aqueous oxalic acid		$xV-SiO_2$ (x =wt.% loading of metal oxide, 5–25%)
Aqueous Cr(NO ₃) ₃		$xCr-SiO_2$ (x =10)
Aqueous Zr(NO ₃) ₄		$xZr-SiO_2$ (x =10)
Montmorillonite K10 (Fluka)	Wet impregnation, air dried, calcined at 723 K	
NH ₄ VO ₃ in aqueous oxalic acid		$xV-K10$ (x =wt.% loading of metal oxide, 5–25%)
Aqueous Cr(NO ₃) ₃		$xCr-K10$ (x =10)
Aqueous Zr(NO ₃) ₄		$xZr-K10$ (x =10)
Wyoming montmorillonite (source clays)	Acid activated with H ₂ SO ₄ , air dried, calcined at 723 K	yMont (y =period of acid activation, 5 min–20 h)
Wyoming montmorillonite, (NH ₄) ₂ [Ce(NO ₃) ₆]	Ion exchange for 38 h (solution changed every 8 h), air dried, calcined at 673 K for 5 h	Ce-Mont
Wyoming montmorillonite (source clays) AlCl ₃ , NaOH	Alumina pillared with polyhydroxy aluminium solution prepared in laboratory by hydrolysis of AlCl ₃ with NaOH, air dried and calcined at 673 K	AlPC(z) (z =OH/Al of the pillaring solution, 0.5–2.25)
Ce-Mont, AlCl ₃ , NaOH	Alumina pillared with polyhydroxy aluminium solution prepared in laboratory by hydrolysis of AlCl ₃ with NaOH, air dried and calcined at 673 K	AlPC (Ce,2)
Silica sol, sodium aluminate, sodium hydroxide, tetra propyl ammonium bromide	Hydrothermal synthesis, 523 K, 30 kg/cm ² , dried at 393 K and calcined at 823 K	NaZSM-5(a) (a =SiO ₂ /Al ₂ O ₃ , 28–150)
NaZSM-5(a), NH ₄ NO ₃	Ion exchange, calcined at 823 K	HZSM-5(a)
Silica sol, sodium aluminate, sodium hydroxide	Hydrothermal synthesis, 523 K, 30 kg/cm ² , dried at 393 K and calcined at 823 K	NaZSM-5(a) (TF) (TF=Template-free)
NH ₄ NO ₃ , NaZSM-5(a) (TF)	Ion exchange, calcined at 823 K	HZSM-5(a) (TF)
HZSM-5(a), V ₂ O ₅ precursors-VCl ₃ , NH ₄ VO ₃ and V ₂ O ₅	Solid state exchange, physical mixture ground for 1 h, calcined in N ₂ at 673 K for 6 h	$bV_2O_5-HZSM-5(a)$ (b =wt.% V ₂ O ₅ , 1–35%)
HZSM-5(a) (TF), V ₂ O ₅		$bV_2O_5-HZSM-5(a)$ (TF)
HZSM-5(a), NH ₄ VO ₃ in oxalic acid	Wet impregnated, calcined at 673 K in air	$bV_2O_5-HZSM-5(a)$ (Imp) (b =12 wt.% V ₂ O ₅)
HZSM-5(a), aqueous VCl ₃	Ion exchange, stirred at 353 K for 7 h (repeated three times)	V ₂ O ₅ -HZSM-5(a) (IE)

used are briefly summed up in Table 4. The catalysts have been well characterized by measurements of surface area, pore size, morphology, crystallinity, acidity measurements by ammonia desorption, ESR, MAS, NMR and the details are described in our earlier papers. Aniline alkylation was carried out in the temperature region 523–723 K and at atmospheric pressure on ca. 500 mg of the sample (powder form) taken in a tubular down flow glass reactor (40 cm × 1.5 cm). Aniline and ethanol mixture (1:5 w/w or 1:10 mole ratio) was fed from the top using a calibrated motorized syringe. The liquid products collected at regular time intervals were analyzed by a gas chromatograph Chemito 3865 under isothermal conditions using a SS column (3 m × 3 mm) with a stationary phase of 10%

Apiezon L treated with 2% KOH on chromosorb AW (80/100). The products identified were *N*-ethylaniline (NEA), *N,N'*-diethylaniline (NN'DEA) and others (mostly C-alkylated products). Conversion of aniline and selectivity of the products is calculated from GC data on ethanol-free basis.

2.1. Temperature effect

Table 5 gives the effect of reaction temperature on conversion of aniline and selectivity of alkyl anilines over silica, montmorillonite K10 and HZSM-5 (28) samples. At 523 and 573 K, the conversion is low and NEA is selectively formed. As the reaction temperature is raised to 673 K, the conversion is increased with

Table 5
Temperature effect^a

Temperature (K)	Oxides ^b				Clays ^b				Zeolites ^b			
	1	2	3	4	1	2	3	4	1	2	3	4
523	3	100	0	0	10	100	0	0	10	100	0	0
573	10	100	0	0	20	80	20	0	15	100	0	0
623	18	95	5	0	45	73	25	2	15	100	0	0
673	35	80	15	5	77	66	24	10	40	70	18	12
723	25	87	10	3	50	75	10	10	14	58	2	40

^a Aniline alkylation at feed rate $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$, $\sim 0.5 \text{ g}$ cat, aniline:ethanol=1:10 mole ratio.

^b 1=% conversion, 2=% selectivity NEA, 3=% selectivity NN'DEA, 4=% selectivity others.

a decrease in the selectivity to NEA and an increase in the formation of NN'DEA suggesting that NN'DEA is formed by further alkylation of NEA. C-alkylanilines are formed at high temperatures (673 and 723 K). Prasad and Rao [67] suggest that the C-alkylanilines are formed by the isomerization of NN'DEA at high reaction temperatures. Similar trend in the conversion pattern is observed over HZSM-5 (28), with different selectivity pattern. NEA is selectively formed upto 623 K and NN'DEA is formed only at 673 K. At 723 K, a good proportion of C-alkylaniline is formed which may be due to the isomerization of NN'DEA.

2.2. Feed rate effect

The effect of varying feed rate is shown in Fig. 3. The clay and silica catalysts gave a maximum conversion at $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ while 26 wt.% V_2O_5 -HZSM-5 showed high conversion at the feed rate of $6 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$. At high contact time (feed rate $6 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$) alcohol is probably dehydrated reducing the effective concentration of the feed thereby lowering the conversion in 10V-K10 and 10V-SiO₂.

2.3. Mole ratio effect

The effect of varying mole ratio of aniline and ethanol is shown in Fig. 4. Increase in conversion is observed on increasing the ethanol content in the reaction mixture upto 1:10 mole ratio. However, excess of ethanol beyond 1:10 mole ratio lowered the conversion because the alcohol probably undergoes side reactions leading to the formation of coke.

2.4. Acidity and alkylation

The studies cited in the review on aniline alkylation suggest that the reaction is an acid catalyzed one and acidity influences the selectivity pattern of the alkyl anilines. Vapor phase aniline alkylation has been studied over different acidic oxides and supported oxides (Table 6) by Narayanan et al. [12–15]. It is observed that the simple oxides are poor catalysts for aniline alkylation. Impregnation with V_2O_5 improves the catalytic activity remarkably, and it is very conspicuous in the case of V_2O_5 -SiO₂. This is attributed to the enhanced acidity which the system acquires due to V^{4+} -O-Si interaction [15]. XRD of $\text{V}_2\text{O}_5/\text{SiO}_2$ samples did not show peaks characteristic of V_2O_5 even upto 25 wt.% loading indicating the absence of large vanadia crystallites of size probably $>4 \text{ nm}$. A comparison of ESR spectra of pure vanadia and silica supported vanadia samples indicate a high dispersion of vanadia over silica. Unsupported vanadia does not show well resolved ESR signals. However, on supporting vanadia over silica, hyperfine splitting of ESR signals (HFS) due to ^{51}V ($I=7/2$) is observed. The signal intensity and HFS increase with vanadia loading from 5 wt.% and reached a maximum around 15–20 wt.% beyond which it tends to diffuse gradually. Hyperfine splitting is an evidence of V^{4+} -O-Si interaction. Ethylation of aniline was also studied over 5–25 wt.% vanadia loaded montmorillonite K10 [29–35]. ESR of V_2O_5 impregnated montmorillonite K10 does not give hyperfine splitting. In the XRD patterns, characteristic peaks of vanadia do not appear upto 10 wt.% loading. It was found that while montmorillonite K10 gave aniline conversion of 77% (reaction temperature: 673 K, $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$),

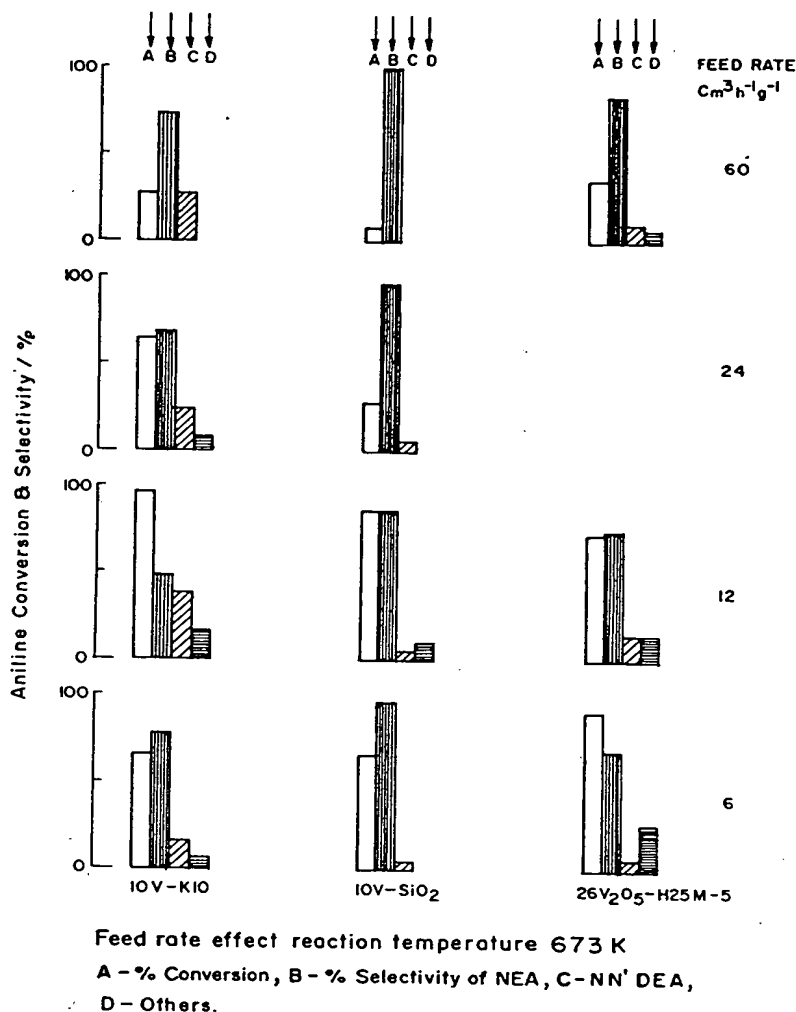


Fig. 3. Feed rate effect over vanadia modified silica, montmorillonite K10 and HZSM-5.

it was as high as 97% over 10V-K10. Further increase in vanadia loading decreases aniline conversion. The relation between total acidity as measured by step-wise temperature desorption (STPD) of ammonia and aniline conversion is shown in Fig. 5. Eventhough addition of V_2O_5 increases acidity of montmorillonite K10, an improvement in conversion is observed only upto 10 wt.% loading. This suggests that the structural factors like dispersion of the metal oxide over the support also play a role in the catalytic activity.

The relation between SiO_2/Al_2O_3 ratio, aniline conversion, alkyl aniline selectivity and the total acidity are shown in Fig. 6. With the increase in SiO_2/Al_2O_3 ratio from 25 to 75, the total acidity and the conversion of aniline were lowered. Beyond SiO_2/Al_2O_3 ratio of 75 both the total acidity and the conversion level off. A direct relation between total acidity and aniline conversion over HZSM-5 of SiO_2/Al_2O_3 ratio 28–150 has been reported by Narayanan et al. [18]. This observation was found to be similar to the earlier studies on alkylation of benzene [63] and alkylation of ethyl-

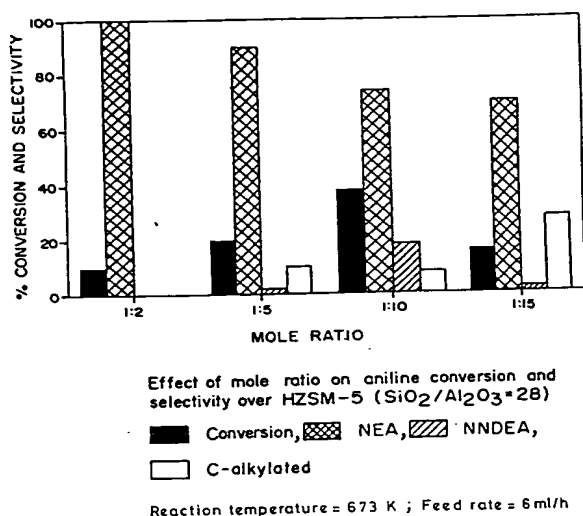


Fig. 4. Mole ratio effect studied over HZSM-5 (28).

benzene [68]. The selectivity to NEA remained almost the same, irrespective of the % aniline conversion and the total acidity. On the other hand, the proportion of NN'DEA was found to increase upto $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 75, inspite of the decrease in total acidity and conversion. This is contrary to the expectation and aniline alkylation being a consecutive reaction, NN'DEA is formed at high conversion. In the case of HZSM-5 synthesized without template, similar relation between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, total acidity and aniline conversion is observed (Fig. 7); however, NN'DEA formation de-

creases with decrease in conversion. These contrasting selectivities of ZSM-5 samples synthesized with and without template suggest that, rather than the total acidity, probably acidity of particular strength and type are responsible for the conversion of aniline and selectivity of alkyl anilines.

The role of acidity favoring the reaction may further be explained as follows. Montmorillonite K10 and silica were modified by impregnating 10 wt.% transition metal oxides, but of different acidic strength and nature viz., Cr_2O_3 , ZrO_2 , V_2O_5 . Chromia is a strong Lewis acid. Zirconia is amphoteric with medium acidity, whereas vanadia is weakly acidic [57]. Auroux and Gervasini [57] have reported that the integral heats of adsorption of ammonia for the three oxides is chromia>zirconia>vanadia. Silica is a very weak Brønsted acid [59] and impregnation of an acidic metal oxide over it is known to enhance the acidity [60]. Montmorillonite K10 is a medium acidic material with Brønsted and Lewis acidity [69]. Vanadia impregnation enhances the acidity of montmorillonite K10, especially in the weak and medium range and also improves aniline alkylation activity of both montmorillonite K10 and silica [12-15,29-35]. Acidity seems to be the main parameter affecting the catalytic activity. Silica being an almost neutral oxide, the effect of an additive on acidity, which in turn influences the catalytic activity, would be more clear on a metal oxide impregnated silica system.

XRD patterns of vanadia and zirconia impregnated samples did not show characteristic peaks of the

Table 6
Aniline alkylation studied over different oxides and supported oxides^a

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	% Aniline conversion	% Selectivity		
			NEA	NN'DEA	Other
V_2O_5	35	35	70	20	10
SiO_2	250	35	81	14	05
ZrO_2	50	30	53	01	46
Al_2O_3	234	55	85	15	-
TiO_2 (A)	140	15	65	05	30
TiO_2 (R)	33	18	65	02	33
$\text{V}_2\text{O}_5/\text{SiO}_2$	204	82	72	21	07
$\text{V}_2\text{O}_5/\text{ZrO}_2$	35	30	28	01	71
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	186	55	80	05	15
$\text{V}_2\text{O}_5/\text{TiO}_2$ (A)	98	33	20	01	79
$\text{V}_2\text{O}_5/\text{TiO}_2$ (R)	59	28	05	01	94

^a Aniline:ethanol=1:10 mole ratio; reaction temperature=673 K; feed rate= $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$; weight of the catalyst=0.5 g.

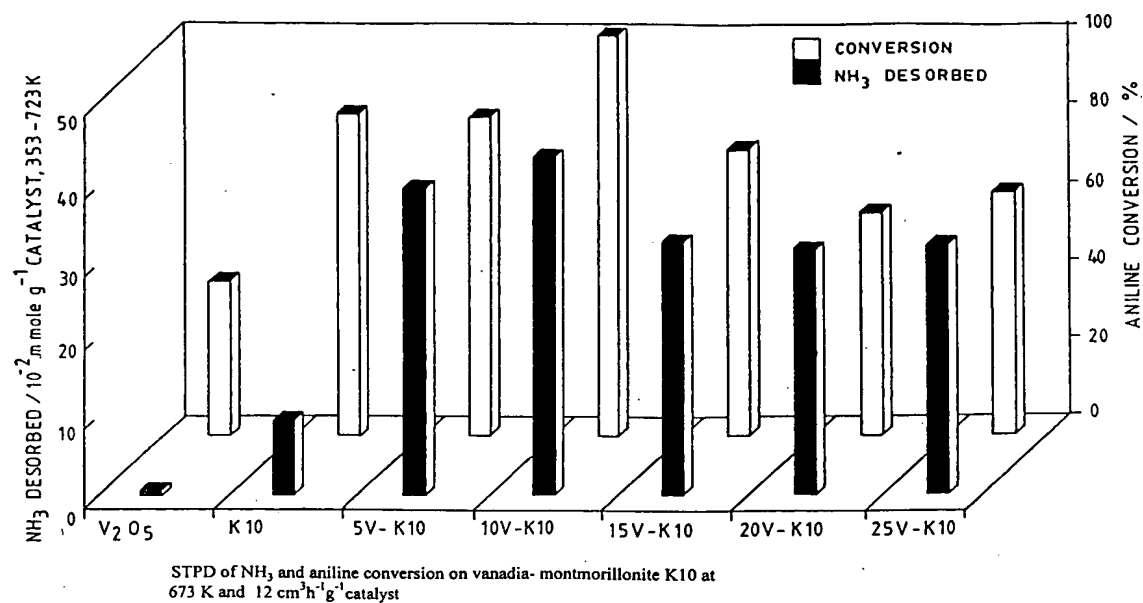


Fig. 5. Relation between total acidity measured by STPD of ammonia and aniline conversion over vanadia impregnated montmorillonite K10 catalysts.

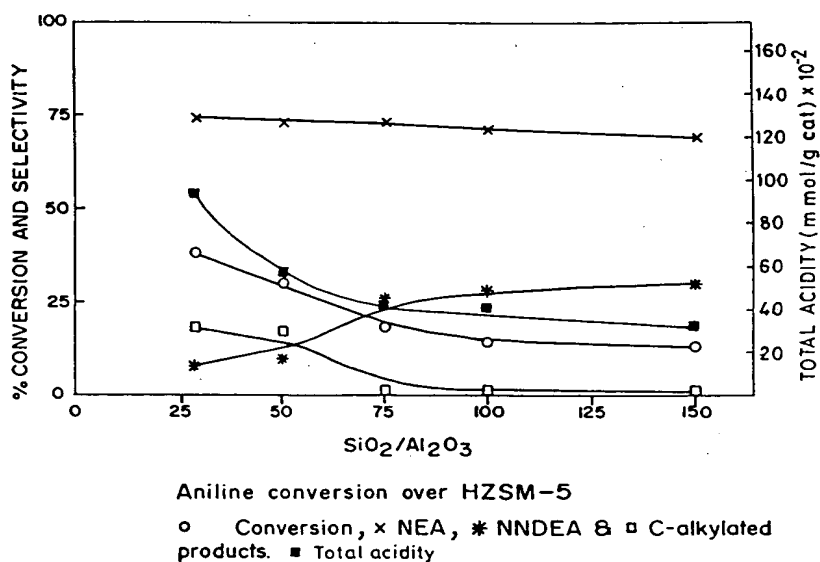


Fig. 6. Relation between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of HZSM-5(T), conversion of aniline and selectivity for alkylated products and total acidity.

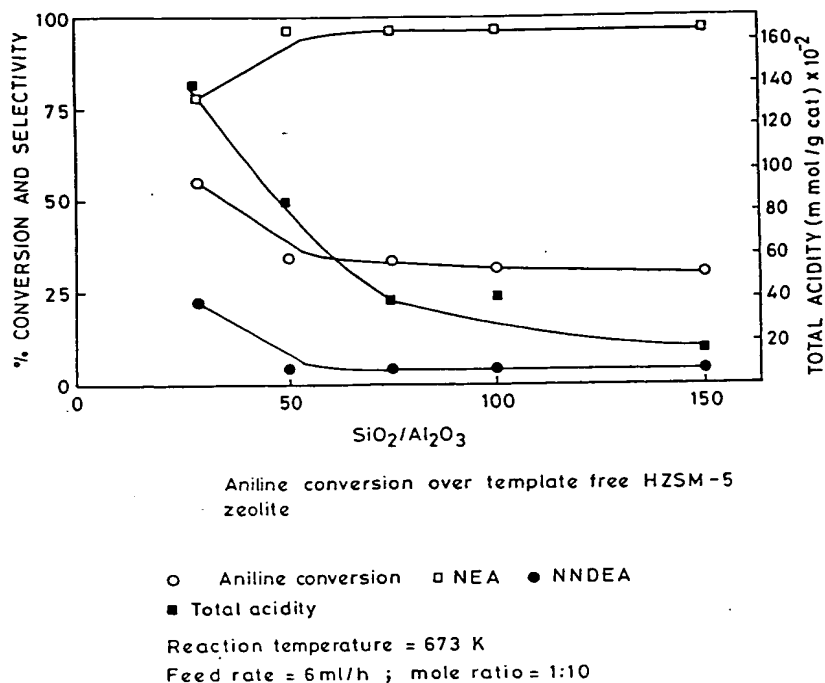


Fig. 7. Relation between SiO₂/Al₂O₃ ratio of HZSM-5(TF), conversion of aniline and selectivity for alkylated products and total acidity.

metal oxides; however chromium impregnated catalysts, showed the corresponding chromia peaks. This suggests that the vanadia and zirconia crystallites dispersed over the support are small and undetectable by XRD. Chromia and zirconia lowered the surface area of silica and montmorillonite K10, and vanadia impregnation has lowered it more than the other oxides (Table 7). A metal oxide when dispersed uniformly

Table 7
Physical parameters of silica and montmorillonite K10 supported oxide catalysts

Sample	Surface area (m ² g ⁻¹)	Acidity/NH ₃ desorbed (10 ⁻⁴ mmol m ⁻²) catalyst 353–723 K
SiO ₂	400	0.6
10V–SiO ₂	308	11.3
10Zr–SiO ₂	348	6.0
10Cr–SiO ₂	363	7.9
Mont K10	275	6.6
10V–K10	149	31.7
10Zr–K10	224	14.1
10Cr–K10	229	16.7

as layers rather than as lumps, block the adsorption sites of the support material lowering the surface area. The conspicuous reduction in surface area of SiO₂ and montmorillonite K10 on vanadia impregnation suggests a uniform dispersion of the oxide over the support. At 10 wt.% loading, zirconia and chromia are probably not well dispersed compared to vanadia. Chromia may be present as large crystallites as evidenced from XRD. Zaki et al. [70], report that beyond 3 wt.% loading of chromia on silica, clusters of chromia are formed and at 10 wt.% metal oxide loading, there is an increase in the amount of surface chromium chromates at the expense of surface polychromates. ESR of the samples suggest that chromium is dispersed as Cr³⁺ over both silica and montmorillonite K10. Zr⁴⁺ is ESR inactive, while vanadium ions are found to be present as V⁴⁺ ions showing hyperfine splitting over silica. ESR of vanadia–montmorillonite K10 system did not give any evidence of V⁴⁺ species.

The impregnated samples show higher acidity than the supports (Table 7). It is expected that chromia, being the strongest acid amongst the three metal

oxides, would contribute maximum acidity to the corresponding supported catalysts. But, contrary to the supposition, the supported chromia showed low acidity. Vanadia supported systems showed high acidity even though vanadia itself is weakly acidic. On dispersing vanadia over SiO_2 or montmorillonite K10, the acidity was found to be in the order $10\text{V-SiO}_2 > 10\text{Cr-SiO}_2 > 10\text{Zr-SiO}_2$ and $10\text{V-K10} > 10\text{Cr-K10} > 10\text{Zr-K10}$, respectively. Microcalorimetric measurements by Le Bars and Auroux [71] have confirmed the higher acidity of vanadia impregnated silica than pure silica or bulk V_2O_5 . Results from discrete vibrational X_α cluster model calculation of $\text{ZrO}_2/\text{SiO}_2$ catalyst have shown an increase in the strength of Brønsted acidity of Si tetrahedra unit when neighbored by a tetrahedral zirconium [58]. ESR spectra and XRD patterns of 10Cr-SiO_2 and 10Cr-K10 have indicated the presence of clusters of chromia over SiO_2 and K10. The surface chromium chromates probably contribute to the acidity. The enhanced acidity in the vanadia systems is probably due to the high dispersion of metal oxide. At 10 wt.% loading, large crystallites of chromia and zirconia may have been formed on the support, functioning more like bulk oxide rather than supported oxides.

Figs. 8 and 9 show the STPD of ammonia on silica and montmorillonite K10 supported samples. The presence of low total acidity, distributed almost equally in the three regions corresponding to 'weak', 'medium' and 'strong' acid sites is revealed. Though K10 has comparatively higher total acidity, the distribution of acid sites is almost equal in all the three ranges. The three oxides contribute to the acidity of the support in varying extent. For example, 10V-SiO_2 records high acidity in 'weak' range. 10Zr-SiO_2 shows high acidity in 'medium' range, while 10Cr-SiO_2 in 'strong' range. The same pattern was observed on montmorillonite K10 supported samples.

Conversion of aniline and selectivity of alkyl anilines on the metal oxide impregnated silica and montmorillonite K10 catalysts are depicted in Figs. 10 and 11. Metal oxide impregnation over silica, increases the conversion of aniline. 10V-SiO_2 catalyst gives higher selectivity to NEA. A comparatively higher selectivity to NN'DEA is observed on 10Zr-SiO_2 and 10Cr-SiO_2 . Among the montmorillonite K10 supported catalysts, the conversion increased only on vanadia impregnation; the other oxides viz., zirconia and chromia do not seem to affect the conversion though there is a slight change in the selectivity pattern.

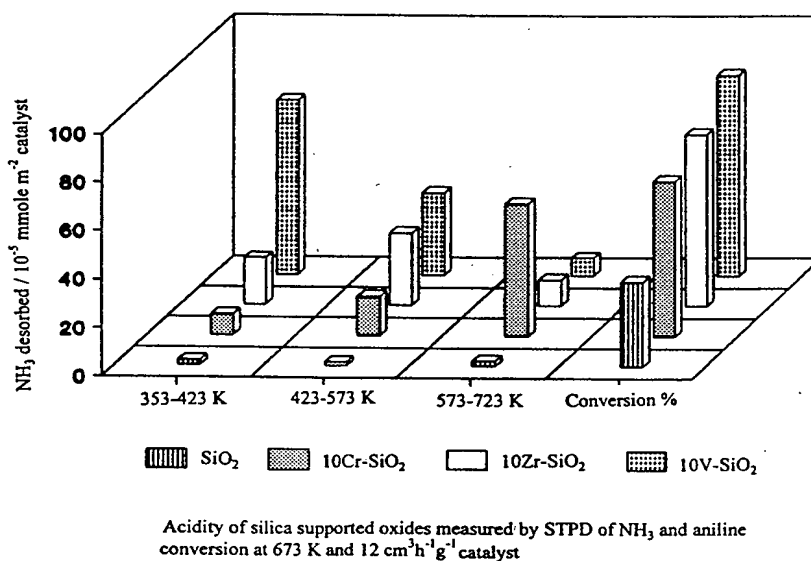


Fig. 8. STPD of ammonia and aniline conversion over silica supported oxides.

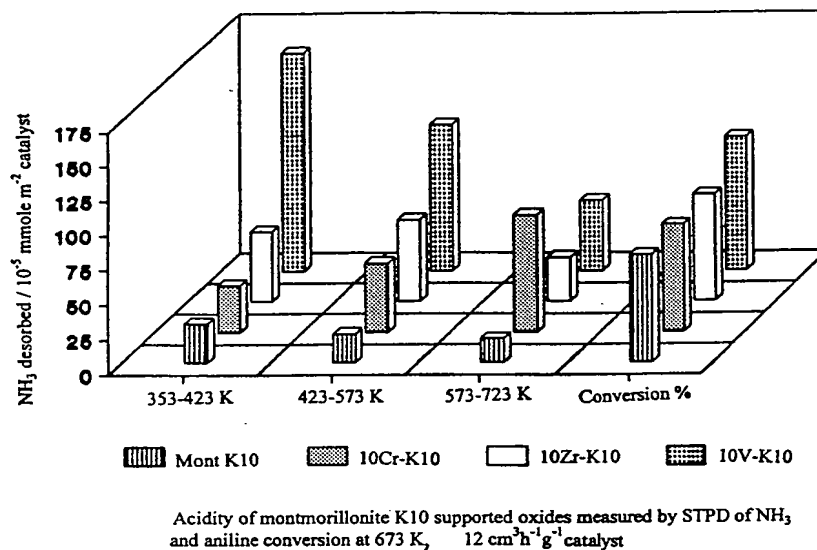
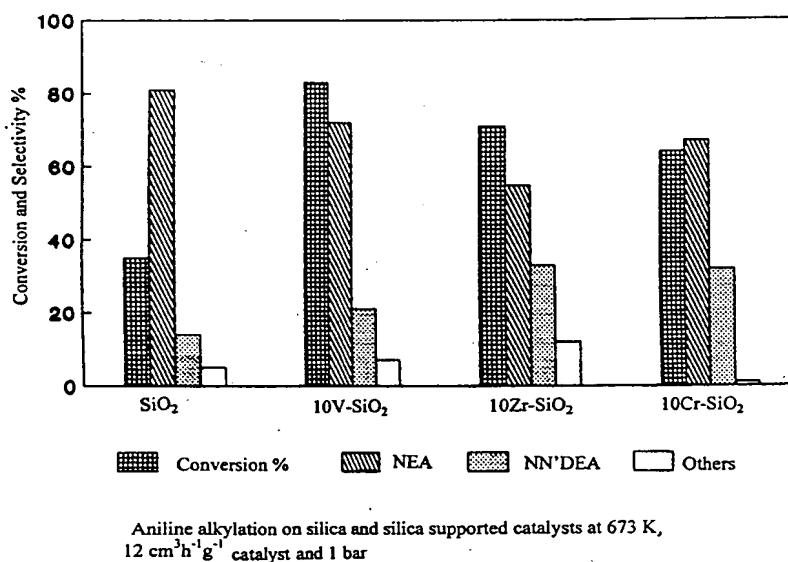
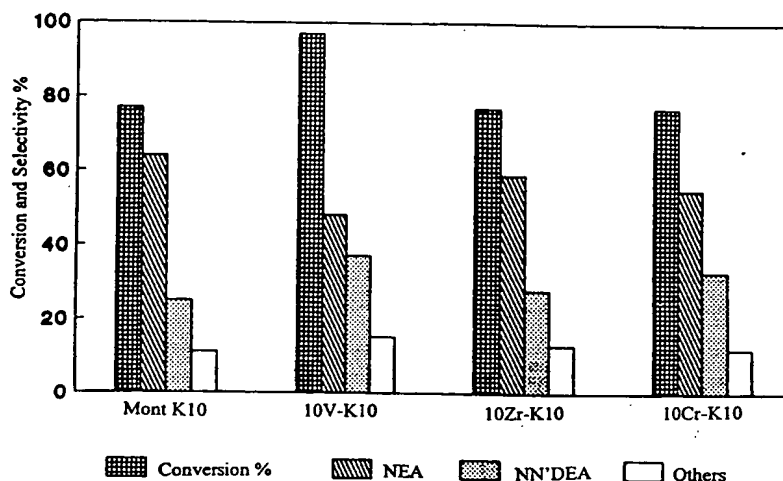


Fig. 9. STPD of ammonia and aniline conversion over montmorillonite K10 supported oxides.

A direct correlation between aniline alkylation and ammonia desorption in the weak and medium ranges, in silica supported systems may be noticed (Fig. 8). Similar observation is noted on montmorillonite K10

based catalysts (Fig. 9). Moreover, the acidity and aniline conversion on K10 supported catalysts reveal that only a certain amount of acidity is required to carry on the reaction and the presence of surplus acidity

Fig. 10. Conversion of aniline and selectivity of alkylanilines for the reaction carried at 673 K and $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ over silica supported catalysts.



Aniline alkylation on montmorillonite K10 and montmorillonite K10 supported catalysts at 673 K and $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$

Fig. 11. Conversion of aniline and selectivity of alkylanilines for the reaction carried at 673 K and $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ over montmorillonite K10 supported catalysts.

does not alter the condition. In such a situation, with a large number of acid sites, there is no quantitative dependence of acidity on conversion. 10Zr-K10 and 10Cr-K10 have almost double the acidity per m^2 of catalyst compared to montmorillonite K10 but this did not change the conversion.

Aniline alkylation is a consecutive reaction. NEA is the primary product which is further alkylated to NN'DEA. Studies on reaction catalyzed by met-allosilicates have suggested that the weak acidity helps *N*-alkylation; medium *N,N'*-dialkylation and the strong C-alkylation [72]. The high selectivity to NEA on 10V-SiO₂ catalyst is because of the presence of a

number of weak acid sites. Amongst the impregnated silica catalysts, 10Cr-SiO₂, having comparatively a low conversion shows higher selectivity to NN'DEA (Fig. 10). The K10 based catalysts (K10, 10Zr-K10 and 10Cr-K10) though have nearly the same conversion, the selectivity to NN'DEA is more on 10Cr-K10 (Fig. 11). As suggested by Woo et al. [66], the high selectivity to NN'DEA may be due to higher acidity of chromia catalysts observed in the range 573–723 K. Recently, Baustista et al. [73] have reported a similar observation that weak to moderate acidity helps *N*-alkylation of aniline over AlPO₄-Al₂O₃ catalysts.

Table 8

Physical parameters and catalytic activity of HZSM-5 samples modified by different methods^a

Vanadium source/method of preparation	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Ammonia desorbed (mmol g^{-1}) $\times 10^{-2}$			Total acidity (mmol g^{-1}) $\times 10^{-2}$	% Aniline conversion	% Selectivity		
		523	623	723			NEA	NN'DEA	Others
V ₂ O ₅ /SSIE	334	50.99	28.76	39.83	119.58	78	74	12	14
VCl ₃ /SSIE	340	50.82	26.79	23.67	101.28	75	81	15	4
NH ₄ VO ₃ /SSIE	338	46.91	28.25	36.18	111.34	82	63	27	10
VCl ₃ /IE	359	52.38	21.31	20.15	93.84	42	79	19	2
NH ₄ VO ₃ /IMP	308	60.44	39.12	27.72	127.28	65	75	8	17

^a SSIE — Solid state ion exchange; IE — Ion exchange; IMP — Impregnation.

The effect of vanadia modification over templated and template-free HZSM-5 and aniline alkylation has also been studied. Table 8 gives acidity and catalytic activity of HZSM-5 samples modified by different methods viz., wet impregnation, ion exchange and solid state exchange using different vanadia precursors. Irrespective of the precursor, 12 wt.% vanadia zeolite prepared by solid state exchange method show high aniline alkylation activity. The low catalytic activity of the conventional ion exchanged sample may be due to incomplete ion exchange. 12 wt.% V_2O_5 impregnated ZSM-5, although has higher acidity than catalysts prepared by other methods, shows low aniline conversion (65%). Thus among vanadia zeolite catalysts prepared by different methods, the ones prepared by solid state exchange gave high conversion.

The XRD patterns of HZSM-5 and vanadia modified HZSM-5 by solid state exchange show that upto 15 wt.% loading, intensity of the peaks corresponding to vanadia are weak; from 18 wt.% V_2O_5 content, the intensity of characteristic vanadia peaks increase with vanadia content suggesting the formation of crystalline vanadia phase on zeolite surface. The addition of vanadia has not changed the surface area of the zeolite significantly upto 18 wt.% of V_2O_5 indicating that vanadia is dispersed as small particles on the surface or entered into zeolite pores (Table 9). ESR of the thermally treated mechanical mixture of V_2O_5 and zeolites at 673 K in N_2 flow gave hyperfine splitting characteristic of V^{4+} species. These signals have been attributed to V^{4+} (VO^{2+}) ions embedded in zeolites and to VO^{2+} in V_2O_5 layers supported on various inorganic carriers [74]. The process of migration and redistribution is dependent on the concentration of Al^{3+} in the zeolite lattice and the conditions

Table 9
Surface area of different wt.% vanadia modified HZSM-5 samples (T and TF)

V_2O_5 loading (wt.%)	Surface area ($m^2 g^{-1}$)	
	T ^a	TF ^b
–	388	321
8.9	368	308
17.8	334	291
26.75	284	270

^a T — Templated zeolites.

^b TF — Template-free zeolites.

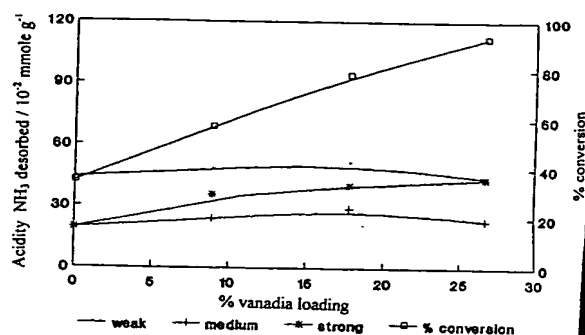


Fig. 12. STPD of ammonia on different wt.% vanadia modified HZSM-5(T) and aniline conversion.

of high temperature treatment [75]. The valence state of V^{4+} in HZSM-5 channels is extremely stable upon redox treatment [76], the cation is not oxidized to V^{5+} state even after heating in air at 1073 K.

Addition of V_2O_5 increases acidity of HZSM-5 in all the three temperature regions (Figs. 12 and 13). In the case of templated samples, aniline conversion showed up dramatically from 45 to 98% on solid state exchange with 28 wt.% V_2O_5 . Template-free samples, on the other hand, showed good aniline alkylation activity even before vanadia modification, and solid state exchange, improved the conversion to 89%. It is reported that the addition of metal ions result in redistribution of the relative number of Brønsted and Lewis acid sites in ZSM-5 [77]. We believe that the addition of metal oxide to HZSM-5 replaces the strong Brønsted protons; the coordinatively unsaturated V^{4+} ions act as Lewis acid sites thereby changing the Brønsted/Lewis

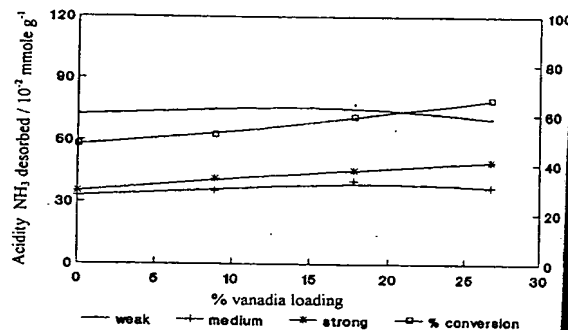


Fig. 13. STPD of ammonia on different wt.% vanadia modified HZSM-5(TF) and aniline conversion.

Table 10
Effect of V_2O_5 on HZSM-5 having different SiO_2/Al_2O_3 ratios

SiO_2/Al_2O_3	Ammonia desorbed in different temperature (K) regions ($mmol\ g^{-1}$) $\times 10^{-2}$			Total acidity ($mmol\ g^{-1}$) $\times 10^{-2}$	% Aniline conversion	% Selectivity		
	523	623	723			NEA	NN'DEA	Others
28	47.9	23.5	35.3	106.2	57	75	10	15
50	42.0	24.3	26.6	92.9	46	56	9	33
150	18.6	12.6	13	44	36	22	–	78

acid sites. Conversion of aniline and selectivity of products over 9 wt.% V_2O_5 modified HZSM-5 with different SiO_2/Al_2O_3 ratio are given in Table 10. Vanadia improves the activity of all the zeolites. NEA and NN'DEA selectivities decrease and C-alkylated aniline selectivity increases on vanadia addition. The increase in strong acidity on vanadia addition could be the reason for high selectivity of C-alkylated products with increase in SiO_2/Al_2O_3 ratio.

The relation between acidity, aniline alkylation and cumene cracking activity of vanadia modified HZSM-5 with increase in vanadia content are brought out in Fig. 14. Alkylation activity is found to increase

with increase in wt.% of vanadia. It has been observed that the weak and medium acid sites are responsible for aniline alkylation activity [32]. It is also reported that the addition of vanadia improves the Brønsted acidity and creates new Lewis acid sites [78] which may be responsible for the higher aniline alkylation activity of V_2O_5 HZSM-5 catalyst. On the other hand, cumene dealkylation reaction which goes mainly on strong Brønsted acid sites [79], is found to be almost the same as on HZSM-5 catalyst. This clearly indicates that the enhanced aniline alkylation activity is due to an increase in the number of Lewis acid sites.

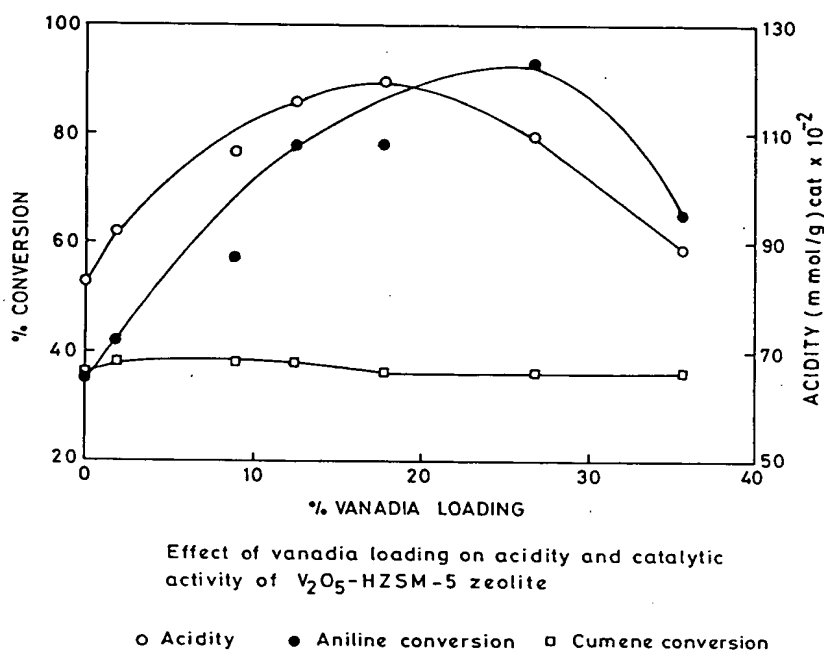


Fig. 14. Relation between acidity, aniline alkylation activity and cumene cracking activity of vanadia modified HZSM-5.

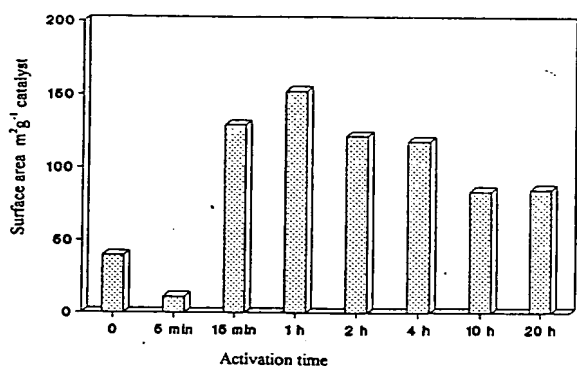


Fig. 15. Changes in surface area of Na montmorillonite due to acid activation.

On the Brønsted and Lewis acid combination, the presence of a large number of Lewis sites has been found to be helpful for the aniline alkylation over acid activated Wyoming montmorillonite [33]. Acid activation brings about changes in the layer structure of the clay causing delamination of the layer structure as well as dealumination. As a consequence, more active sites are exposed resulting in enhanced surface area. Aluminium leaching results in increase in mesoporosity [80]. Fig. 15 depicts the changes in surface

area of Na montmorillonite due to acid activation. Surface area of Na montmorillonite increases from 40 to $130 \text{ m}^2 \text{g}^{-1}$ on activation for 15 min and for 1 h it reaches a maximum of $152 \text{ m}^2 \text{g}^{-1}$. Acid treatment for 4 h, reduces the surface area only slightly and on prolonged acid activation, say for 10 h, the surface area drops to $96 \text{ m}^2 \text{g}^{-1}$. Acidity of Na montmorillonite and acid activated Na montmorillonite is given in Fig. 16. The acid activated montmorillonite samples have more acidity than the pristine clay. As the period of acid activation increased there is a drastic increase in the weak acidity which reaches a maximum for 4 h acid activation and decreases slightly on further activation for 10–20 h. Acidity in the medium range increases slightly on 15 min acid activation and on further treatment there is no change. The change in the strong acidity range also goes through a maximum for 2–4 h activation, but the change is less conspicuous. Generally, the trend in the acidity change on acid activation of Na montmorillonite as measured by STPD of ammonia is weak >> medium > strong.

The IR spectra of pyridine adsorbed samples suggest that the pristine clay has a large number of Lewis sites while acid activated samples have a higher proportion of Brønsted acid sites [81]. Lewis acidity arises from isomorphous substitution of Al^{3+} for Si^{4+} in

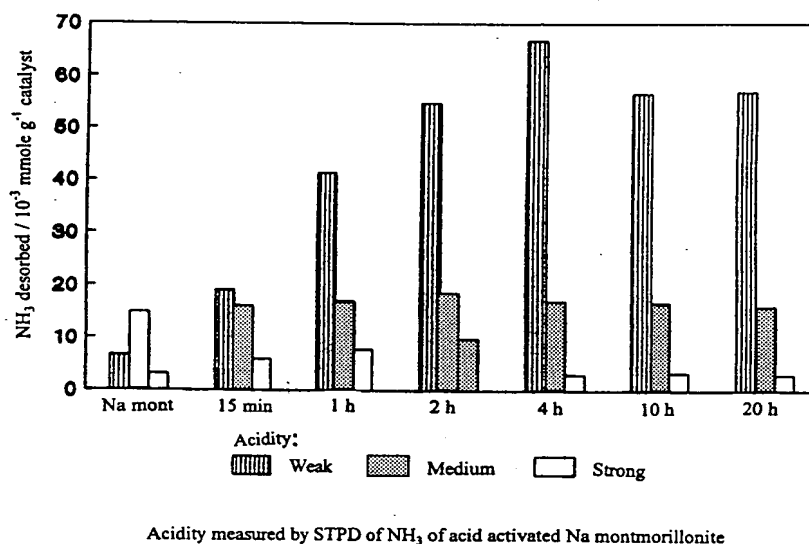
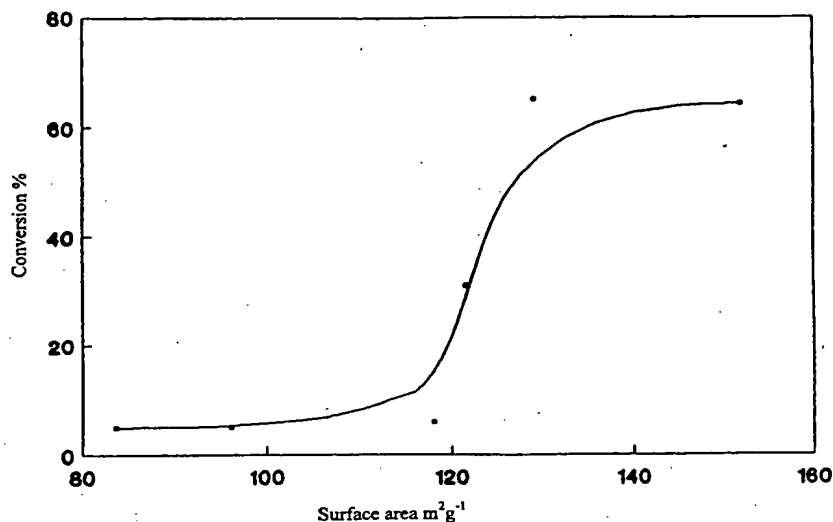


Fig. 16. Changes in acidity of Na montmorillonite and acid activated Na montmorillonite as measured by STPD of ammonia.



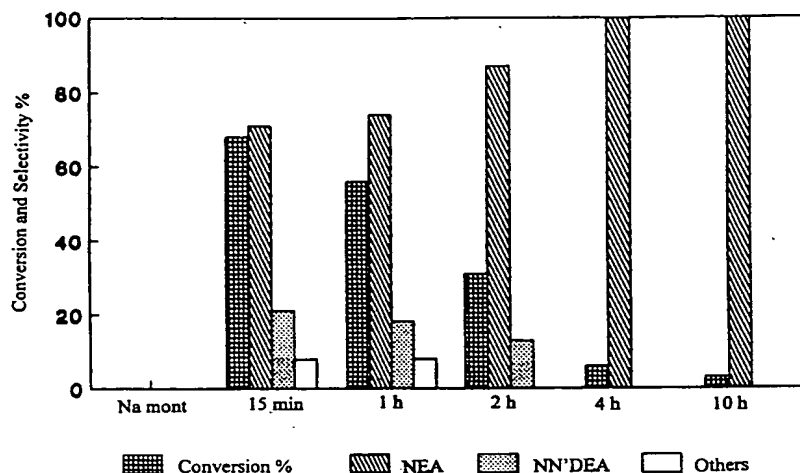
Dependence of aniline alkylation on surface area of acid activated Na montmorillonite

Fig. 17. Dependence of aniline alkylation over surface area of the catalysts.

tetrahedral sites. Acid activation leaches aluminium from the lattice and reduces the number of Lewis sites. Presence of acidic cations (mainly Al^{3+}) in the interlamellar region of acid activated montmorillonite and existence of protons on its matrix increase the Brønsted acidity [81]. Fig. 17 describes the dependence of aniline alkylation on the surface area of the catalysts. Initially the aniline conversion was found to increase with increase in surface area and it reached 70%, when the surface area of the catalyst is about $130 \text{ m}^2 \text{g}^{-1}$. Further increase in surface area does not seem to affect the catalytic activity. Conversion of aniline and selectivity pattern of alkyl anilines over the acid activated samples is given in Fig. 18. Na montmorillonite is inactive for the reaction. 15 min acid activated sample showed the highest aniline conversion of 70%. On further acid activation, the aniline conversion reduced gradually to almost 5% on the sample activated for 10 h. The selectivity is found to be more for NEA over all the samples. Low aniline conversion on Na montmorillonite samples activated for more than 1 h in spite of their possessing considerable acidity (weak and medium range) and surface area may be because of lowered Lewis acidity on prolonged acid activation.

2.5. Structural factors and aniline alkylation

A comparison of aniline alkylation activity over zeolites with different structural and acidic properties is given in Table 11. In spite of the differences in acidities, HX, HY and HZSM-5 show almost the same activity and selectivity with a marginal difference in the case of HZSM-5. H-mordenite, although possesses more acid sites in all the three regions compared to others, does not show catalytic activity commensurating with either total acidity or strong acidity. Kikhtyanin et al. [25], reported that the wide pore zeolites although possess strong Brønsted and Lewis acid sites, do not show any increase in the alkylation of aniline with methanol. In fact, strong acidity may be disadvantageous, as it may cause cracking of alcohol, reducing availability of alcohol for the reaction. These results indicate that, the three-dimensional framework zeolites (HZSM-5, HX, HY) are more suitable for aniline alkylation than the unidimensional framework H-mordenite. The formation of *N*-alkylanilines probably takes place in the intersections of the zeolite channels. The unidimensional nature, added to the presence of strong acid sites may lead to easy deactivation and blocking in H-mordenite by the coke formed from the cracking of alcohol.



Aniline alkylation over acid activated Na montmorillonite carried out at 673 K, $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ and 1 bar

Fig. 18. Conversion of aniline and selectivity pattern of alkylanilines over acid activated samples.

Investigations of aniline conversion carried out on pillared montmorillonite highlight the structural influence of the catalyst. Pristine montmorillonite possesses low surface area (about $39 \text{ m}^2 \text{ g}^{-1}$). N_2 adsorption on clays represents the external surface area and the surface available in the meso and macropores. The low surface area is because of the possibility of face to face stacking of the layers when the clay is dried and degassed. On pillaring, the pillars support the sheets and prevent them from collapsing during the drying process. The galleries that are formed on calcination, serve as micropores. The physical parameters of the prepared alumina pillared montmorillonite is given in Table 12. From the shift of the characteristic peak cor-

responding to $d(001)$ spacing and the intensity of the peak, it is evident that the pillaring has taken place. The $d(001)$ spacing of the pristine clay samples increased from 12.62 to 16.72 Å and 17.38 Å in AlPC(2) and AlPC(Ce,2), respectively. In the case of Ce-Mont, which is an ion exchanged sample (not pillared), interlamellar spacing increased upto 18.70 Å (Table 12). However, the characteristic peak is observed to be of low intensity indicating comparatively low $d(001)$ order in the sample. The N_2 adsorption isotherm on the pillared samples is of Type I which is characteristic of microporous materials in which multilayer adsorption of N_2 is sterically hindered. Isotherm of Ce-Mont appears to be intermediate between Types I and IV.

Table 11

Acidity and aniline conversion over different zeolites

Zeolite sample	Ammonia desorbed (mmol g^{-1}) $\times 10^{-2}$ in different temperature regions (K)				Conversion (%)	% Selectivity		
	523	623	723	Total		NEA	NN'DEA	Others
HM	57.3	16.8	86.32	160.42	2	100	—	—
HZSM-5	25.03	9.18	7.85	42.06	35	89	8	3
HY	17.05	16.09	5.43	38.57	31	80	20	—
HX	17.09	2.66	0.59	20.34	30	80	18	2

Table 12
Physical parameters of Na Montmorillonite and modified montmorillonites

Catalyst	Interlamellar distance $d(001)$ Å	BET surface area ($\text{m}^2 \text{g}^{-1}$)	External surface area (A_{ext}) ^a ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ^b ($\text{cm}^3 \text{g}^{-1}$)	Micropore volume (V_{mi}) ($\text{cm}^3 \text{g}^{-1}$) ^b
Na-Mont (source clays)	12.6171	27.43	18.81	0.0348	0.004
Ce-Mont	18.7054	98.60	101.34	0.1052	Negligible
AlPC(2)	16.7227	169.56	38.85	0.0949	0.0638
AlPC(Ce,2)	17.3806	184.12	100.23	0.1282	0.0404

^a Calculated from the t -plot.

^b N_2 condensation at $P/P_0=0.95$ in the pores of diameter <400 Å.

Surface area calculated by following BET equation is given in Table 12. Surface area of Na montmorillonite increased from 27.43 to $169.56 \text{ m}^2 \text{g}^{-1}$ on alumina pillaring (AlPC(2)) and to $184.12 \text{ m}^2 \text{g}^{-1}$ on alumina pillaring of Ce exchanged sample (AlPC(Ce,2)). Increase in surface area on pillaring is expected, since the process creates regular porosity. Surprisingly, Ce exchange also enhanced the surface area to $98.60 \text{ m}^2 \text{g}^{-1}$. However, the increase in surface area on Ce exchange is not as high as in the case of pillared samples. Apparently the ion exchange and subsequent calcination changed the stacking pattern of the pristine clay. The process might have resulted in a layer arrangement similar to the house of cards structure.

Total pore volume of the samples is measured by condensation of N_2 adsorbate at $P/P_0=0.95$ in the pores of diameter <400 Å by single point method (Table 12). On pillaring, the total pore volume increased from $0.0348 \text{ cm}^3 \text{g}^{-1}$ in the pristine clay to $0.0949 \text{ cm}^3 \text{g}^{-1}$ in the case of AlPC(2) and $0.1282 \text{ cm}^3 \text{g}^{-1}$ in the case of AlPC(Ce,2). However, there is not much variation in the total pore volume of the montmorillonite samples pillared with different OH/Al ratio. It is reported that [82] the micropores contribute to about 60–70% of the total pore volume. Ce-Mont despite a low $d(001)$ order like the pristine sample, gave considerable total pore volume of $0.1052 \text{ cm}^3 \text{g}^{-1}$.

The linear branch of the isotherm above $P/P_0=0.5$ is used [83] for the measurement of the external surface area (A_{ext}) and the micropore volume (V_{mi}). The parameters are derived using t -plot of DeBoer [84] or α_s -plot of Sing [85]. The mesopores in clays are mainly the interparticle voids [83] and in pillared clays, mesopores mainly contribute to the A_{ext} . The external surface area (A_{ext}) of the samples is calculated from the t -plot and given in Table 12. In the case

of Ce-Mont, A_{ext} is observed to be almost the same as BET surface area suggesting that mainly mesopores in the sample contribute to the active sites. Micropore volume of the samples is given in Table 12. Pillaring increased the micropore volume from $0.004 \text{ cm}^3 \text{g}^{-1}$ in Na montmorillonite to $0.064 \text{ cm}^3 \text{g}^{-1}$ in AlPC(2) and to $0.04 \text{ cm}^3 \text{g}^{-1}$ in AlPC(Ce,2). Theoretically, the maximum value for micropore volume in alumina pillared smectites is reported [86] to be nearly $0.12 \text{ cm}^3 \text{g}^{-1}$. Ce-Mont gave negligible micropore volume.

Pillaring increases acidity of the clay. The process by propping up the clay layers, exposes the Brønsted and Lewis acid sites of the layers. Furthermore, the pillars add acid sites to the already existing hydroxyl groups and to Al. Alumina pillars are known to increase especially the Lewis acidity [87]. Among the alumina pillared samples prepared with different OH/Al ratios, the variation of acidity in the weak and medium range is not conspicuous (Fig. 19); whereas, the acidity as measured by desorption of NH_3 in the temperature region 573–723 K, increased with OH/Al ratio and reached a maximum for the sample with OH/Al=1.5. The total acidity and its distribution in the three temperature regions for AlPC with OH/Al=1.5, 2 and 2.25 is almost the same. Comparison of STPD of ammonia of Ce-Mont, AlPC(2), AlPC(Ce,2) shows (Fig. 20) that the pillared samples have more strong acidity than Ce-Mont. The total acidity of the two pillared samples is almost the same ($75.6 \times 10^{-2} \text{ mmol g}^{-1}$ — AlPC(2) and $69.8 \times 10^{-2} \text{ mmol g}^{-1}$ — AlPC(Ce,2)) but the distribution of acidity in three temperature ranges is different. In the case of AlPC(2) the weak and medium acidity are almost equal but the strong acidity represented by the ammonia desorption in the temperature range 573–723 K is comparatively

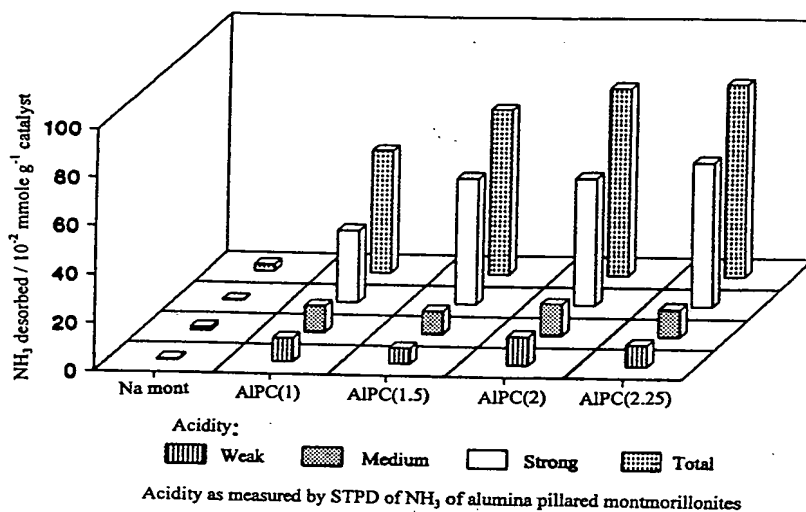


Fig. 19. Acidity as measured by STPD of ammonia of alumina pillared montmorillonites.

more. On the other hand, in the case of AIPC(Ce,2) the acidity is almost equally distributed in the three regions. Almost equal total acidity of the samples AIPC(2) and AIPC(Ce,2) but different distribution of acidity in the three temperature regions suggests that Ce ions though do not contribute to the acid-

ity, lead to a structurally dissimilar alumina pillared clay.

Na montmorillonite is found to be inactive for aniline ethylation (Table 13). Over the alumina pillared montmorillonites, with the increase in OH/Al ratio from 1 to 2.25, the conversion decreased from 76 to

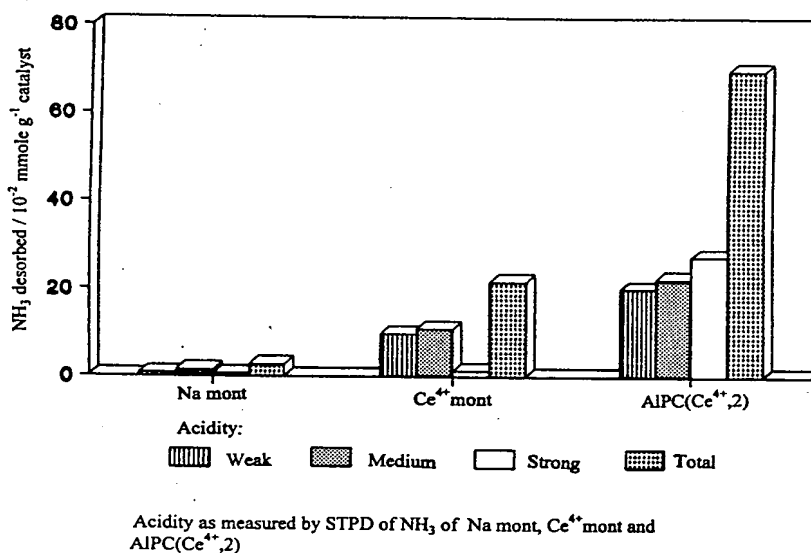


Fig. 20. Acidity as measured by STPD of ammonia of Ce-Mont, AIPC(2) and AIPC(Ce,2).

Table 13

Aniline ethylation carried out over Al pillared montmorillonites at 673 K, feed rate $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ and 1 bar

Clay sample	% Conversion of aniline	% Selectivity		
		NEA	NN'DEA	Others
Na-Mont (source clays)	–	–	–	–
Ce-Mont	55	52	40	7
AlPC(1)	76	47	29	24
AlPC(1.5)	61	50	26	24
AlPC(2)	51	65	28	7
AlPC(2.25)	50	63	27	10
AlPC(Ce,2)	81	51	30	19

50%. Aniline alkylation studies [32] over modified silica and montmorillonite K10 suggests that, though the presence of a certain amount of acidity, especially in weak and medium range, are essential for the reaction, surplus acidity does not affect the conversion. Different alumina pillared samples, despite possessing considerable surface area and almost same weak and medium acidity showed low aniline conversion. Among all the alumina pillared samples, aniline conversion was the lowest (51%) over AlPC(2). Low aniline conversion (55%) over Ce-Mont may be due to its comparatively low surface area ($98.60 \text{ m}^2 \text{ g}^{-1}$) and total acidity ($21.65 \times 10^{-2} \text{ mmol g}^{-1}$). However, the corresponding alumina pillared form i.e. AlPC(Ce,2) gave aniline conversion of 81% (surface area: $184 \text{ m}^2 \text{ g}^{-1}$ and total acidity: $69.79 \times 10^{-2} \text{ mmol g}^{-1}$). These observations suggest that the porosity of the pillared clays affect the conversion of aniline but not on the selectivity pattern of the alkyl anilines.

2.6. Alkylation activity over microporous solids

Physical parameters and aniline conversion of the microporous solids studied are given in Table 14. XRD of vanadia modified HZSM-5 indicates that the

crystalline structure of the zeolite is intact inspite of the solid state exchange. The modification resulted in the formation of VO^{2+} species over the surface and in the channels of the zeolite. So basically, the channel structure of the zeolite is unaffected. The decrease in the aniline conversion (76–50%) over alumina pillared montmorillonites with different OH/Al ratio (1–2) suggests that the increase in microporosity with the increase in the OH/Al ratio is probably the reason. But 93% aniline conversion over V_2O_5 -HZSM-5 which has smaller micropores than alumina pillared montmorillonites rules out the probability of restricted diffusion of aniline and alkylanilines due to small pore diameter. The difference in the conversion between the pillared montmorillonites and zeolites may therefore be due to the diffusion problems associated with the irregular structure of the former compared to zeolites. ZSM-5 has regular structure of micropore openings leading into the channels.

In the case of pillared species, micropores are the pores lined by clay layer surface on two sides and the two pillars on the other two sides. In between the layers, the pillars are not regularly arranged; so there is no formation of a channel like regular path for the molecules to diffuse freely in pillared clays. In AlPC(1), when the OH/Al=1, the pillar density is less, since the concentration of the polymeric cation is low [88]. This facilitates easy movement of the reactant and product molecules and explains the high conversion among the prepared AlPC catalysts. Low conversion in the case of AlPC(2) is due to the hindered movement of reactant and product molecules as the pillar density is reported to be highest when OH/Al ratio is 2. Alumina pillaring of Ce ion exchanged montmorillonite was carried out to obtain a pillared clay with regular pillar arrangement [88]. On the contrary, AlPC(Ce,2) has almost the same micropore volume as AlPC(2) and it has higher external surface area than AlPC(2) suggesting the presence of more mesopores in the sample. A large number

Table 14

Physical parameters and % aniline conversion over microporous solid acids

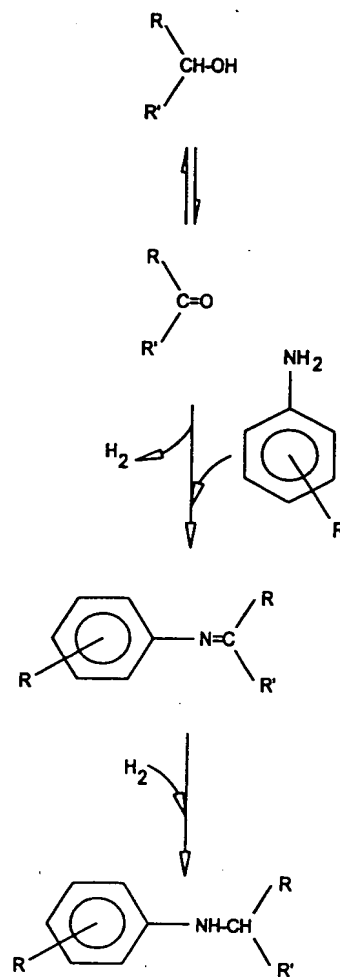
Catalyst	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Total acidity measured by desorption of ammonia ($\text{mmol NH}_3 \text{ g}^{-1} \text{ cat}/10^{-2}$)	Micropore diameter (\AA)	% Conversion of aniline
27 wt.% V_2O_5 -ZSM-5 (28)	284	109.3	~5	93
AlPC (OH/Al=2)	169.56	75.6	22.38	51

of mesopores indicate less pillar density and less obstructions for the reactant and product molecules explaining the conversion of 81% over AIPC(Ce,2).

2.7. Mechanism of alkylation

The orientation effect in the aromatic rings is closely related to the electropolar nature of the previously introduced group. The electropositive, neutral and slightly negative groups that contribute to the basic properties direct the substituent towards *ortho*- and *para*-positions. The electronegative groups, strengthen the acidic properties of the aromatic compound and direct the substitution at the *meta*-position. The amino group ($-\text{NH}_2$) bound to the aromatic ring exerts *ortho/para* orientation effect. This is because of the delocalization of the unshared pair of electrons over the amine group into the benzene ring. As a result the *ortho* and *para* sites of the ring become most susceptible to the electrophilic substitution and the expected major product is the *ortho* and/or *para* C-alkylated aniline. Due to the adsorption of aniline on the surface of the catalyst, alkylation usually yields *N*-alkylated products. The catalyst also plays a role in releasing the electrophile from the alkylating agent namely, alcohol. Alkylation with alcohols and haloalkanes is analogous to that of olefins which takes place by generation of electrophiles from heterolysis of carbon–oxygen or carbon–halide bonds [89]. Rusek [16], Rice and Kohn [17] have proposed that, in the presence of hydrogen, *N*-alkylation of aniline takes place by dehydrogenation of alcohol to carbonyl, followed by the formation of an imine which is finally hydrogenated to alkylaniline (Scheme 1).

Prasad and Rao [67] have studied aniline alkylation over $\text{AlPO}_4\text{-5}$ catalysts with a parallel study on reactions of *N,N'*-dimethylaniline. They suggest that during methylation of aniline, the formation of *N*-methyl aniline is favored at low temperature. This is subsequently methylated to NNDMA which undergoes isomerization to *N*-methyl toluidine at high reaction temperatures. Our observations also suggest that aniline alkylation is a consecutive reaction. Based on the results of aniline alkylation carried out over a set of catalysts, we have proposed the reaction mechanisms (22, 30) for the formation of primary product viz., NEA over the solid acid catalysts on the assump-

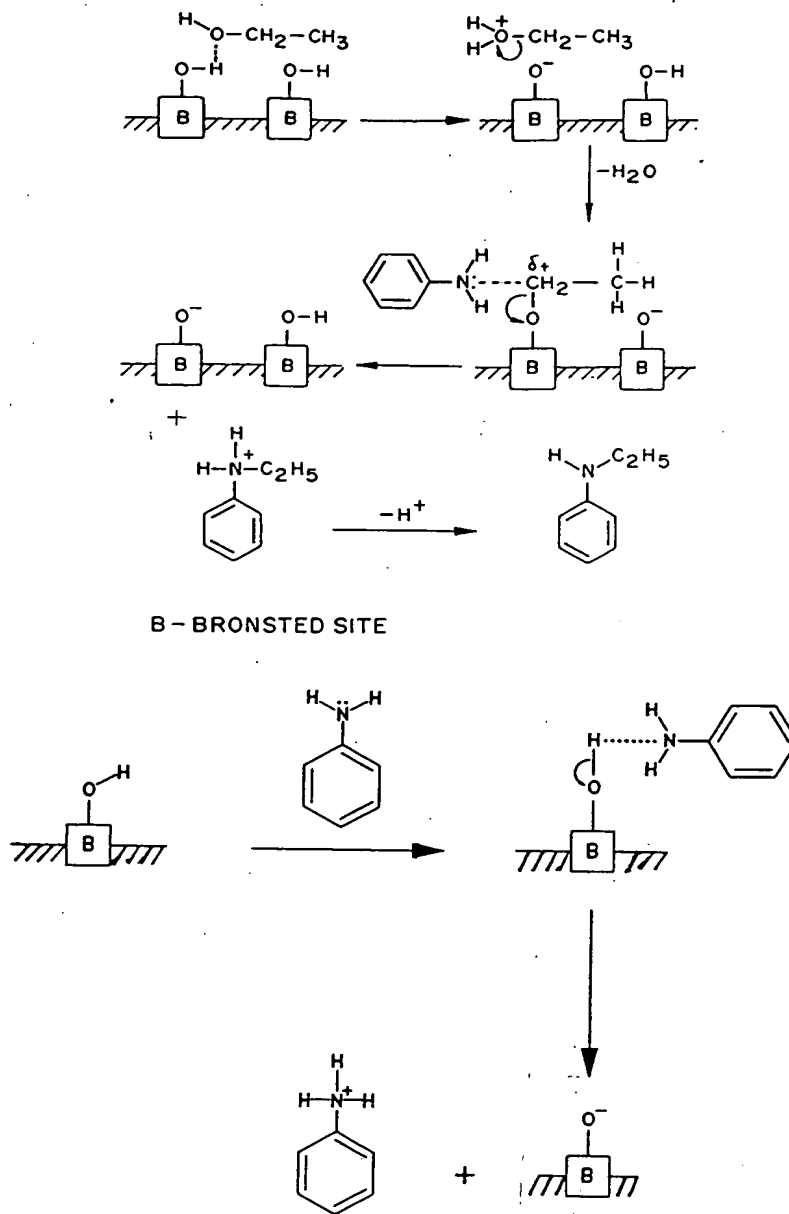


Scheme 1. Mechanism for aniline alkylation in reducing medium.

tion that the secondary and C-alkylated products are formed from NEA. Formation of NEA seems to be a facile reaction under acid catalyzed vapor phase conditions. Mechanism is hypothesized under different conditions of the catalyst containing:

1. only Brønsted acid sites;
2. only Lewis acid sites;
3. both Brønsted and Lewis acid sites.

Scheme 2 depicts aniline alkylation on catalyst having only Brønsted acid sites and is very similar to the situation present on silica catalyst. Weak Brønsted acidity of silica has been well established.



Scheme 2. Aniline alkylation involving only Brønsted acid sites.

[59]. Dehydration of alcohol involved in the reaction helps in maintaining slight acidity of silica even at high reaction temperature of 673 K. Brønsted acidity helps the reaction by dehydrating the alcohol to give

carbocation. On the otherhand, aniline gets protonated to give anilinium ion bringing down the rate of reaction (Scheme 2). This may be the reason for a comparatively low aniline alkylation activity of silica

Table 15

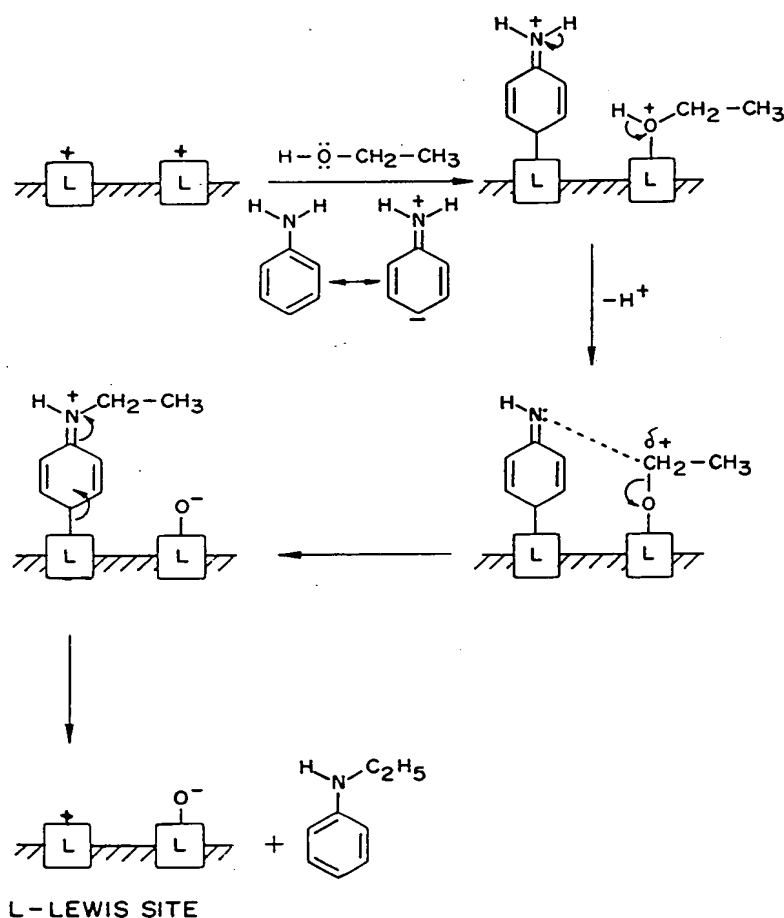
Aniline alkylation activity of silica, montmorillonite K10 and vanadia modified silica and montmorillonite K10^a

Catalyst	Total ammonia desorbed (mmol g ⁻¹) × 10 ⁻² (353–723 K)	% Conversion	% Selectivity		
			NEA	NN'DEA	Others
SiO ₂	2.41	35	81	14	5
Mont K10	20.28	77	64	25	11
10V-SiO ₂	34.88	83	72	21	7
10V-K10	47.10	97	48	37	15

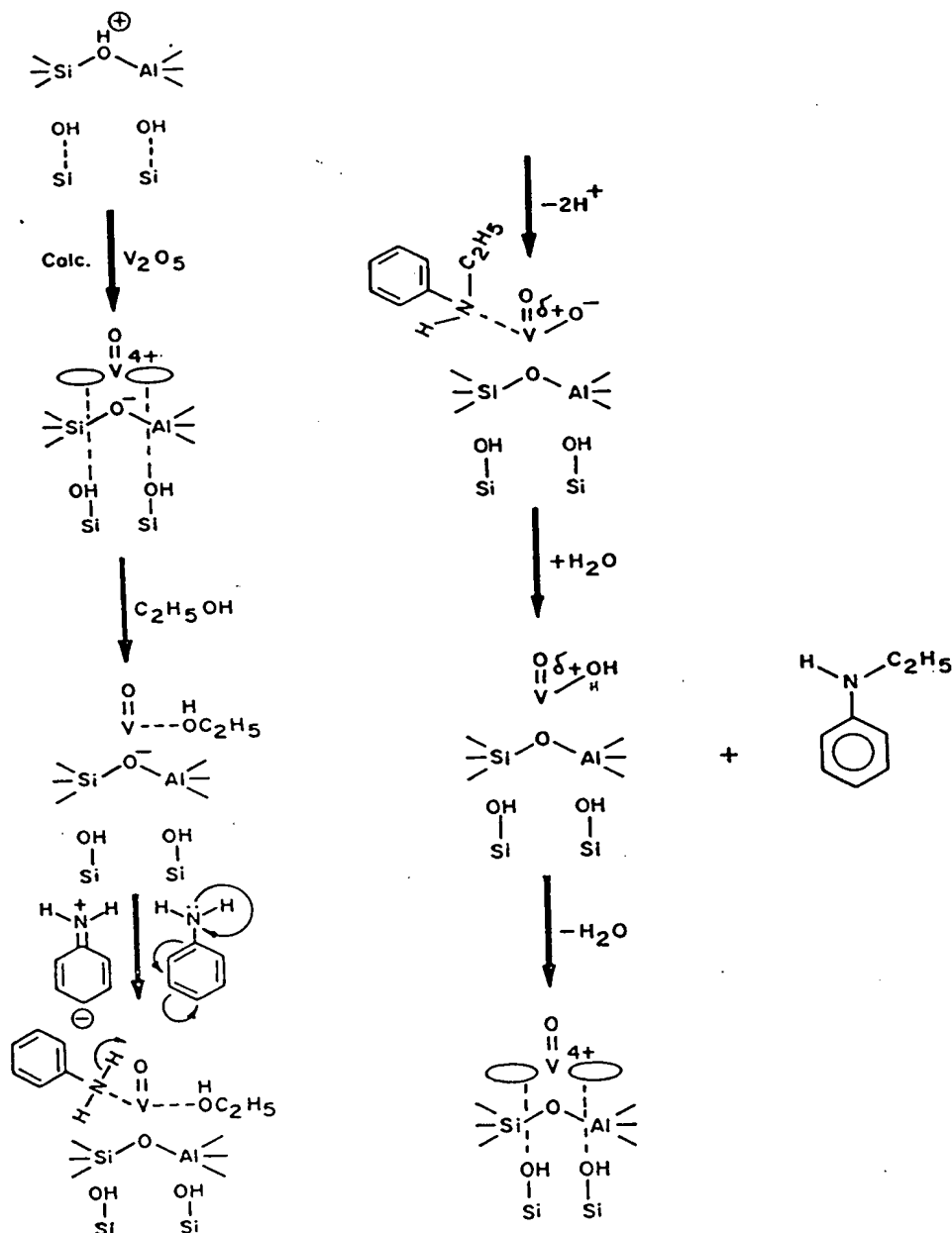
^a Aniline alkylation at 673 K, feed rate 12 cm³ h⁻¹ g⁻¹, 1 bar; weight of the catalyst=0.5 g, aniline:ethanol=1:10 mole ratio.

(Table 15). However, the absence of deactivation of silica surface for 4 h indicates that the anilinium ion may be washed down by the excess of alcohol used in the feed. The activation of ethanol is initiated by hydrogen

bonding between Brønsted hydroxyl proton and oxygen of alcohol. It leads to the alcohol protonation and dehydration, releasing the carbocation. Formation of NEA on silica surface may be explained by the elec-



Scheme 3. Aniline alkylation over Lewis acid sites.



Scheme 5. Aniline alkylation over vanadia modified zeolites.

Ammonia adsorption by infrared spectroscopy using the diffuse reflectance mode (DRIFT) of V_2O_5/SiO_2 catalyst has shown it to be a medium acidic material possessing both Lewis and Brønsted acid sites of

equal strength [78]. These sites seem to be of suitable strength and number, for aniline alkylation, enhancing the conversion. Montmorillonite K10 an acid activated clay is reported to possess both Brønsted

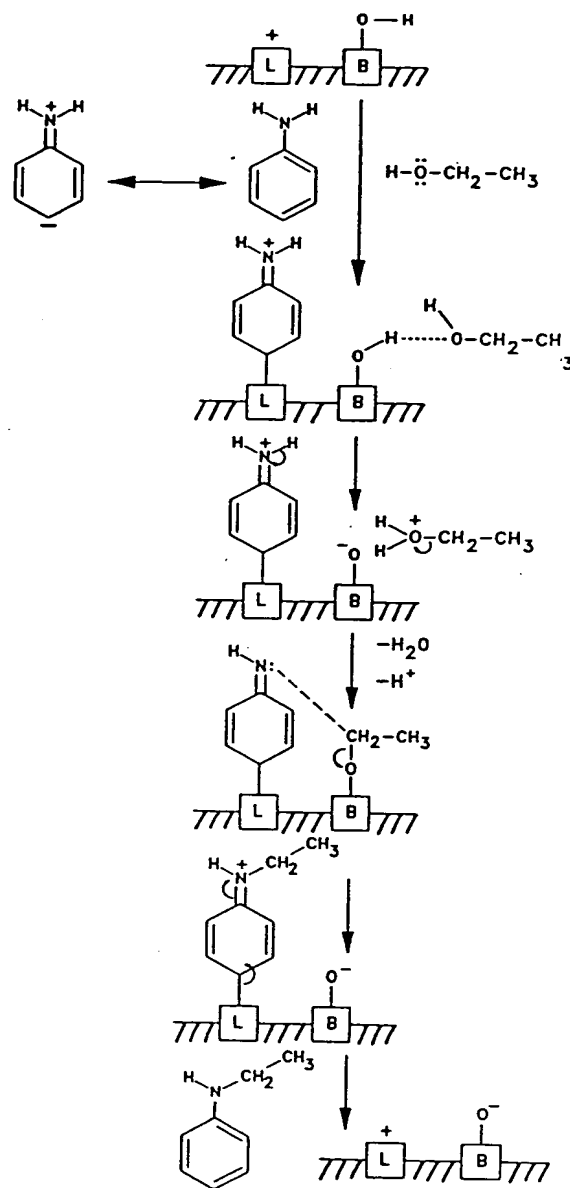
trophilic substitution of the released carbocation, on the unadsorbed base molecule, i.e., aniline (Scheme 2).

Scheme 3 describes the reaction on a catalyst surface possessing only Lewis acid sites. Aniline being a stronger base than ethanol gets adsorbed preferentially on the Lewis site. However, the presence of a large excess of alkylating agent, does not rule out the possibility of ethanol getting adsorbed on the acid sites. Having a catalyst system with exclusively Lewis sites is rather unlikely under the reaction conditions involving dehydration of alcohol. Even if the catalyst does not possess Brønsted hydroxyls to start with, it may eventually develop them during the course of alkylation in presence of H_2O released during the reaction.

Mechanism of aniline alkylation on a catalyst system containing both Lewis and Brønsted sites is depicted in Scheme 4. Aniline being a stronger base than ethanol, preferentially gets adsorbed on Lewis sites, while high electronegativity of oxygen of ethanol leads to hydrogen bonding with hydroxyl protons of Brønsted sites. Protonation of alcohol, dehydration and subsequent formation of ether of the released carbocation with the conjugate base of Brønsted acid site may follow. On the Lewis site, the adsorbed aniline loses a proton to balance the positive charge developed on the nitrogen. The high electronegativity of oxygen in the ether linkage results in the development of a partial positive charge on the alkyl side chain, initiating heterolytic cleavage of polar O–C bond and the shift of alkyl carbocation to nitrogen.

Aniline conversion on silica, montmorillonite K10, 10V– SiO_2 and 10V–K10 and the total acidity of catalyst are given in Table 15. 10 wt.% vanadia impregnated silica (10V– SiO_2), montmorillonite K10 and 10 wt.% vanadia impregnated montmorillonite K10 (10V–K10) possess both Lewis and Brønsted acidity [69,71]. Aniline alkylation on these catalyst systems is proposed to go by Scheme 4. V_2O_5 is weakly acidic. STPD of ammonia measurement indicated acidic sites on V_2O_5 which desorbed ammonia only in the temperature region 353 to 423 K. Weak acidity on bulk V_2O_5 has been reported [71] and it shows a low catalytic activity. However, when V_2O_5 was impregnated on SiO_2 , a well dispersed catalyst system with vanadia probably in (4+) oxidation state was obtained [15] helping high catalytic activity.

Vanadia impregnation over SiO_2 shows almost 14 times more acidity than SiO_2 (Table 15). Creation of



Scheme 4. Aniline alkylation over Brønsted and Lewis acid sites.

new acid sites with higher strength, on V_2O_5 impregnated SiO_2 , than pure silica or bulk V_2O_5 have been identified by microcalorimetric measurements [71]. Infact, deposition of various oxides on silica seems to enhance the acidity of the catalyst system [60].

and Lewis acid sites. Vanadia impregnation increases acidity of montmorillonite K10 [29–32]. However, montmorillonite K10 itself seems to have sufficient acidity as measured by STPD of ammonia and it shows good aniline conversion of 77% and hence addition of vanadia did not improve alkylation to a great extent.

The mechanism of aniline alkylation over zeolites is different because of the presence of active sites involved in the reaction are inside the channels of the microporous structure. The diffusivity of the reactants and products play a role in the selectivity for a particular alkylated product. The aniline conversion was found to be low over ZSM-5 zeolites compared to oxides and clays probably because of the restricted diffusion of aniline and alkylanilines. As in the case of silica and montmorillonite K10 catalysts, the selectivity was found to be more for *N*-ethyl aniline suggesting that the pattern of adsorption of the reactant molecules over the active sites is similar. Over vanadia modified HZSM-5, vanadia is dispersed as VO^{2+} ions due to the interaction of V_2O_5 and zeolite. Oxygen of $\text{V}=\text{O}$ is bound to only to the vanadium ion and is in the *z*-direction, while the others are the framework oxygens present in the *x*–*y* plane. These oxygens may be from Si and Al or from two Si atoms. The mechanism of aniline alkylation over vanadia modified zeolites is given in Scheme 5. The initial step in aniline alkylation over vanadia modified zeolites is activation of ethanol by V^{4+} ions. In the next step, aniline is adsorbed on V^{4+} species followed by dehydration, formation of carbocation and subsequently the shift of carbocation to *N* moiety of aniline forming *N*-ethylaniline. V^{4+} once again helps in the formation of the cation and the process continues.

Template-free zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3=28$, synthesis duration=168 h) gave more aniline conversion compared to HZSM-5 synthesized with template (41 and 23%). Template free zeolites are known to be rich in Lewis acid sites [19,20]. This observation made us to conclude that of the Brønsted and Lewis acid sites combination, presence of more number of Lewis sites seem to be beneficial for the reaction [20]. A comparatively low aniline conversions were observed on acid activated Wyoming montmorillonite treated for more than 2 h inspite of their possessing considerable surface area and acidity. This is because acid activation

lowers Lewis acidity by leaching Al from the octahedral layers [33].

3. Summary

Any catalyst development and catalysis should tie up with environmental considerations. Friedel–Craft catalysis is an important reaction and uses conventional Lewis acids. Safe solid acid catalysts are the answer to the unacceptable systems. Aniline alkylation over solid acid catalysts comprising of oxides, mixed oxides, supported oxides, zeolites, supported zeolite, clays and the modified systems have been reviewed from the point of view of catalytic efficiency and selectivity patterns for alkyl anilines. Modifications have been made either by impregnation, solid state exchange as in the case of zeolites, ion exchange, acid activation and pillaring as in the case of clays. The importance of structural differences among the pristine catalysts and modified catalysts on stability, activity and selectivity variation is brought out. The role of modifiers and the method of modification on reactant and product selectivity from the point of view of acidity changes and diffusion limitation are discussed. The dependence of acidity, in general, on aniline alkylation activity and the extend of involvement of weak, medium and strong acid sites, as estimated by step-wise temperature programmed desorption (STPD) of ammonia by bracketing the desorption temperature has been reasonably established.

An acceptable correlation between total acidity and aniline alkylation may be found within a set of catalyst systems; however, it may not be applicable to the acidity–alkylation activity relationship of two different sets or type of catalysts. Most of the solid acids have their inherent acidity which is required for acid catalysis. The modification by oxide doping either by impregnation or ion-exchange or by solid state exchange bring about usually an increase in the acidity of the pristine material. In the case of vanadia loading on an oxide, a solid–solid interaction of the type $\text{V}-\text{O}-\text{Al}$ or $\text{V}-\text{O}-\text{Si}$, $\text{V}-\text{O}-\text{Zeo}$ takes place and because of the good dispersion of vanadia and the exposure of V^{4+} species the acidity component of the catalyst increases and hence the activity. The interaction and dispersion depend on the solid oxide and the type of oxide additive. ESR studies support the formation of

V^{4+} ions species on oxide support. This is also true in the case of clays as well, however to a lesser extent. The acid activation of clays introduces enough acidity due to dealumination and delamination and hence vanadia does not improve alkylation to commensurate with the increase in the acidity. No such interaction between vanadia and clay has been noticed from the ESR spectra. Alkylation requires only some acidity to start with especially if the alkylating agent is alcohol and it goes via carbonium ion mechanism. Once the activity starts the acid sites are self generating using the water generated during the reaction.

The mechanism proposes that aniline alkylation takes place simultaneously on Brønsted and Lewis sites present side by side. It is also believed that only weak to moderate acidity favor the reaction and the presence of a certain minimum number of acid sites is enough to trigger the reaction. Any excess number of acid sites even if present will not be involved in the reaction and will be superfluous. Strong acidity, on the other hand, if present will only deactivate the catalyst by coking due to cracking of the alcohol and there by making it non-available for alkylation. The presence of more Lewis sites are preferred for the reaction.

From the enormous information gathered on the reaction over several solid acid catalysts, it is clear that *N*-alkylation of aniline is a facile reaction. The reaction is believed to be consecutive or sequential and follows the order: Aniline \rightarrow NEA \rightarrow NN'DEA \rightarrow Others. A moderate reaction conditions and low conversion levels favor the selective formation of the secondary amine viz., NEA. High temperature and high conversion levels favor further alkylation and intramolecular transformations. It is possible to selectively synthesize *N*-alkylated products by controlling the reaction parameters and the acidity nature of the catalysts.

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Montmorillonite as a versatile solid acid catalyst for *tert.*-butylation of resorcinol

Sankarasubbier Narayanan*, K.V.V.S.B.S.R. Murthy

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

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Abstract

The liquid phase alkylation of resorcinol with *tert.*-butyl alcohol was carried out over HZSM-5, HY, HM, MCM-41, alumina, montmorillonite-K10 and modified montmorillonite-K10 (mont.-K10). The major products of this reaction on these catalysts were 4-*tert.*-butyl resorcinol and 4,6-di-*tert.*-butyl resorcinol. Unmodified montmorillonite-K10 shows a very low conversion compared to modified montmorillonite. The conversion in terms of catalytic activity increases in the order modified mont.-K10 \gg HZSM-5 $>$ HY $>$ HM $>$ MCM-41 $>$ Al₂O₃ $>$ mont.-K10. The activity and selectivity differences between the catalysts are explained based on their physical properties and acidity differences. The study brings out the significantly high butylation activity of modified montmorillonite-K10 compared to zeolite and oxide catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Butylation of resorcinol; 4-*tert.*-Butyl resorcinol; 4,6-di-*tert.*-Butyl resorcinol; Solid acid catalysts; Acidity correlation

1. Introduction

Butylation of dihydroxybenzenes is an industrially important reaction as the products of this reaction, butylhydroxybenzenes are useful materials in the synthesis of antioxidants, polymer stabilizers and in the treatment of mitochondrial respiration ailments. Most of the information in connection with the alkylation of dihydroxybenzenes using mineral acids are available in the form of patent literature [1]. This reaction is a Friedel-Crafts class of catalysis and generally carried out using sulfuric acid, phosphoric acid, and aqueous citric acid as catalysts [2,3]. Alkylation of aromatic compounds on modified clays have been described [5–8]. We have been using several solid acid materials, such as alumina, vanadia, zeolites, hy-

drotalcite and clays as catalysts for the alkylation of aniline and phenol [9–18]. The economics associated in the separation process and the present day's stringent environmental concerns on the disposal of spent homogeneous catalysts make it difficult to proceed with them any more. Because of the importance of the reaction and due to lack of enough available information in the open literature, we have taken the study of alkylation of dihydroxybenzenes with *tert.*-butanol, in particular resorcinol. The study assumes importance, especially in the content of enviro-catalysis as we are interested in using solid acids, which are environmentally benign in place of the conventional and hazardous mineral acid catalyst. So far there is no report available to our knowledge on the use of solid acid catalysts for the *tert.*-butylation of resorcinol. In the present study, we report, for the first time, our observation on the versatile catalytic behavior of modified montmorillonite-K10 (mont.-K10) clay for

* Corresponding author. Fax: +91-40-7173757.

E-mail address: snarayanan@iict.ap.nic.in (S. Narayanan).

Table 1
Physical properties of the solid acid catalysts

Catalyst	Description	Pore-size (Å)	SiO ₂ /Al ₂ O ₃	Surface area (m ² g ⁻¹)
Mont.-K10	Fluka	–	–	275
Al ₂ O ₃	Harshaw	0.6	–	190
MCM-41	Lab preparation	–	–	980
HM	CBV 20 A	7	20	540
HY	CBV 400	7.5	5.2	640
HZSM-5	CBV 3020	5.6	30	400

this reaction in comparison with zeolites, oxides and sulfuric acid.

2. Experimental

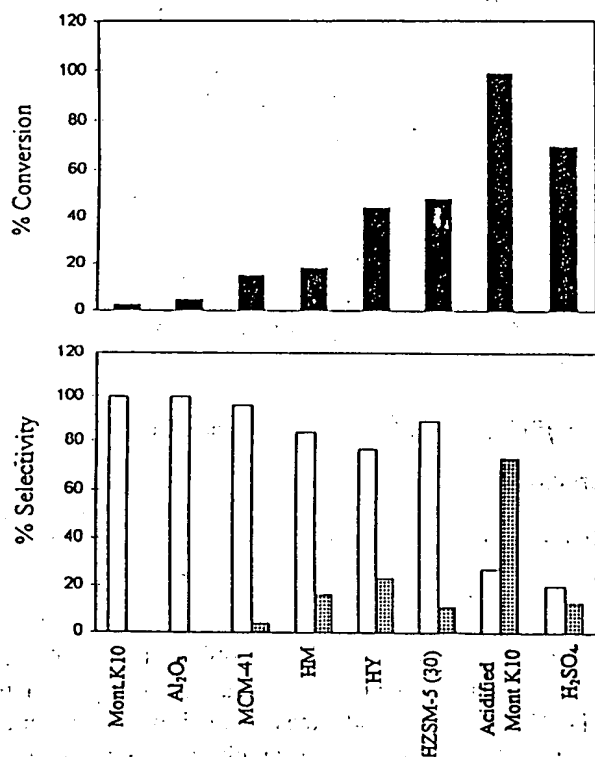
Experiments were carried out over HZSM-5, HY, HM, MCM-41, mont.-K10, modified mont.-K10, Al₂O₃ and H₂SO₄ catalysts. Al₂O₃, zeolites and mont.-K10 are of commercial origin. MCM-41 was prepared according to the literature procedure [4], and was crystalline as verified by XRD. The material was calcined in air at 773 K for 12 h to remove the template and surfactant. Mont.-K10 (Fluka) was modified by refluxing with 30% sulfuric acid for 60 min and filtered. The solid material was washed with distilled water until the filtrate became pH = 7. All the materials were characterized by XRD, FTIR and acidity measurements involving stepwise temperature programmed desorption of ammonia on a Micromeritics Pulse Chemisorb 2700 by bracketing the temperature of desorption. The details of acidity measurements are already described in our earlier paper [10]. Surface area, SiO₂/Al₂O₃ ratio and pore-size description details on the catalysts are given in Table 1.

The alkylation reaction was carried out by taking 1 g of resorcinol, 2.8 ml of *tert*.-butyl alcohol and 200 mg of the catalyst powder in a round bottom (RB) flask. The molar ratio of resorcinol to *tert*.-butyl alcohol was 1:3. The weight ratio of resorcinol to catalyst was 1:5. The reaction mixture was refluxed at 353 K for 8 h. The effect of reaction temperature was studied on the conversion of resorcinol and selectivity of products. In the case of sulfuric acid catalyzed reaction, the molar ratio of resorcinol:*tert*.-butyl alcohol:sulfuric acid was maintained at 1:3:0.4. Here again, 1 g of resorcinol and 2.8 ml of *tert*.-butyl alcohol were taken in a

50 ml RB flask and were refluxed with 0.22 ml of 1 M sulfuric acid at 353 K for 8 h. After completion of the reaction, 5 ml of methanol was added to make the end product mixture less viscous and easy for filtration. The product mixture was analyzed by a Chemito 8510 gas chromatography (GC) using 20% SE-30 column, coupled with FID. The products mixture was separated by silica-gel chromatography and were identified using standards. GC-MS and ¹H-NMR spectra of the products confirm them to be 4-*tert*.-butyl resorcinol and 4,6-di-*tert*.-butyl resorcinol. ¹H-NMR data for 4-*tert*.-butyl alcohol is δ = 1.4, s, 9H (*tert*.-butyl), 5.75, brs, 2H (OH), 6.2, dd, 1H (Ar-H), 6.34, dd, 1H (Ar-H), 7.1, d, 1H (Ar-H), and for 4,6-di-*tert*.-butyl resorcinol is δ = 1.4, s, 18H (*tert*.-butanol), 4.65, s, 2H (OH), 6.0, s, 1H (Ar-H), 7.1, s, 1H (Ar-H).

3. Results and discussion

The reaction is carried out by refluxing a mixture of *tert*.-butanol and resorcinol using zeolites and modified mont.-K10 as catalysts. The product analysis revealed that 4-*tert*.-butyl resorcinol and 4,6-di-*tert*.-butyl resorcinol were formed indicating that butylation took place selectively at 4 and 6, positions of resorcinol. The differences in the conversion of resorcinol and selective formation of 4-*tert*.-butyl and 4,6-di-*tert*.-butyl resorcinol over various solid acid catalysts along with the findings on the sulfuric acid catalyzed reaction is shown in Fig. 1. Unmodified or non-acid treated mont.-K10 clay shows a very low conversion (<5%) where as the modified or the acid treated mont.-K10 shows a very high conversion (>95%). The conversion in terms of catalytic activity increases in the order modified mont.-K10 >> HZSM-5 > HY > HM > MCM-41 > Al₂O₃ >

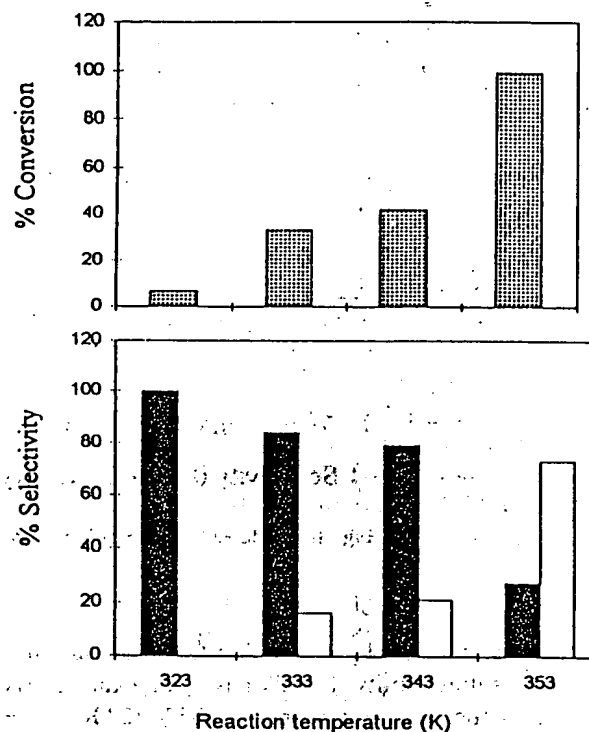


(■) Conversion of resorcinol (□) 4-*tert*-butyl resorcinol (▨) 4,6-di-*tert*-butyl resorcinol.

Fig. 1. Liquid phase *tert*-butylation of resorcinol at 353 K; resorcinol/*tert*-butanol = 1:3 mole/mole; resorcinol/catalyst = 1:5 wt./wt.

mont.-K10. H₂SO₄ gives a resorcinol conversion higher than all other catalysts except of course acidified mont.-K10. The low conversion behavior over zeolites compared to acidified mont.-K10 might be attributed to the diffusion limitations due to its small pore-structure (Table 1).

The influence of temperature on alkylation of resorcinol with *tert*-butanol over acidified mont.-K10 is depicted in Fig. 2. The conversion of resorcinol increases from 7 to 99% as the reaction temperature increases from 323 to 353 K. At 323 K, the selectivity to monoalkylation is 100% even though the conversion is only 7%. With the increase of reaction temperature the dialkylated resorcinol is also formed and it surpasses the selectivity of the monoalkylated resorcinol at 353 K. This is also an indication that the monoalky-



(▨) conversion of resorcinol. (▨) 4-*tert*-butyl resorcinol (□) 4,6-di-*tert*-butyl resorcinol

Fig. 2. Effect of reaction temperature on *tert*-butylation of resorcinol over acidified mont.-K10.

lation precedes the dialkylation and the high temperature facilitates the formation of dialkylated product.

The changes in conversion and selectivity on the *tert*-butylation of resorcinol over acidified mont.-K10 is shown in Fig. 3. The conversion varies slightly with time. It can be seen that the selectivity for 4-*tert*-butyl resorcinol is always higher than the selectivity for 4,6-di-*tert*-butyl resorcinol. It looks like there is a kind of an equilibrium pattern on conversion and selectivity during the time period studied.

The acidity of the catalyst samples was measured by stepwise temperature programmed desorption of ammonia (STPD). The relative weak, medium and strong acidity of the catalysts namely modified mont.-K10, mont.-K10, HY and HZSM-5 is depicted in Fig. 4. As explained in our earlier paper [10], the desorption of ammonia was done at three predetermined

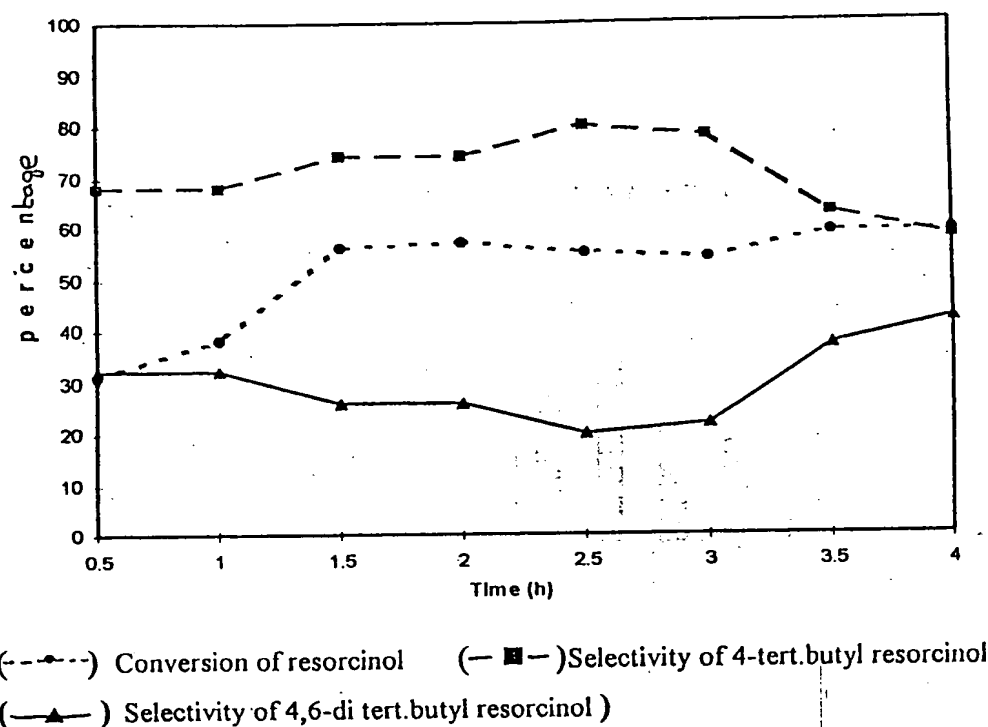


Fig. 3. Alkylation of resorcinol with *tert.*-butyl alcohol: effect of initial reaction time.

temperature regions, by bracketing the lower and upper temperature limits. In this case, for example, A represents the temperature region 353–423 K, B = 423–523 K and C = 523–623 K, respectively. The three relative strength of acidity are measured on the assumption that the strongly held ammonia responsible for strong acidity will be desorbed at higher temperature and the weakly chemisorbed ammonia on a relatively weak acid sites, which will desorb at a low temperature. The total acidity is the sum of all the three acidity as measured by the total ammonia desorbed. The Bronsted and Lewis acid sites present on the surface of the modified clay help in the release of the carbocation, $(\text{CH}_3)_3^+$, from *tert.*-butanol and facilitates the reaction [9,13,19–21]. The acidity of the modified mont.-K10 seems to be sufficient to give a good resorcinol conversion of >95%. Eventhough, HY, HZSM-5 catalysts have a relatively strong acidity, only weak to moderate acidity seems to be responsible for the reaction especially if we use *tert.*-butanol

as an alkylating agent. Similar observations have been made by us in the alkylation of aniline using methanol [13]. Very strong and excess acid sites are not beneficial and they only help to crack alcohol and hence it will not be available for the reaction [20]. The mechanism of formation of carbocation over montmorillonite clays and formation of alkyl aniline has been reported by Narayanan et al. [13,21]. Another interesting observation is that, sulfuric acid, a commonly used Friedel-Crafts catalysts, shows only 70% conversion for this reaction under the same experimental conditions. Thus we have a modified mont.-K10 clay which is even superior to conc. Sulfuric acid for alkylating resorcinol.

The selectivity of the products based on GC analysis is also shown in Fig. 1. When the conversion is very low (especially below 10%) mont.-K10 and alumina yield mono-*tert.*-butyl resorcinol as the only product. As the conversion increases the second product namely, 4,6-di-*tert.*-butyl resorcinol starts appearing.

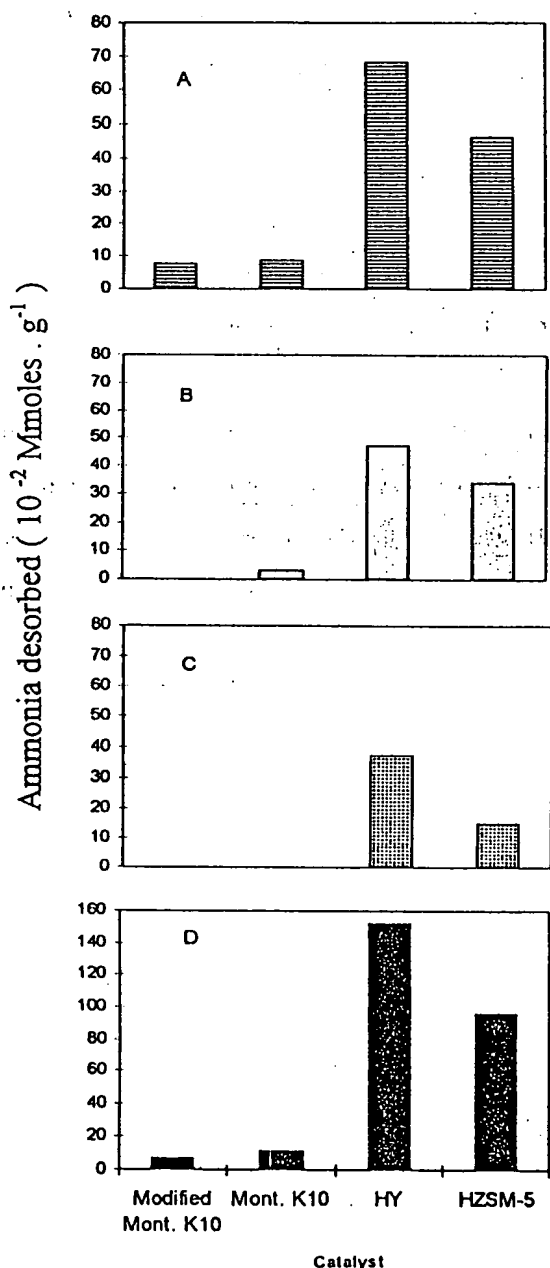


Fig. 4. STPD of ammonia: measured between A = 353–423 K, B = 423–523 K, C = 523–623 K and D = total (353–623 K).

The acidified mont.-K10 with over 95% conversion gives more dialkylated resorcinol than the monoalkylated. The product distribution seems to be dependent on the acidity and pore-size of the catalysts. Acid

activation of pristine clay not only affects the acidity, but also enhances the surface area and mesoporosity of the clay [22]. The pore-size of the acidified mont.-K10 is expected to be much larger compared to the pristine clay due to delamination and widening of interlamellar spacing. In the case of sulfuric acid, even though the conversion is much higher than zeolites, alumina and unmodified clay, the selectivity of mono and dialkylated products is low indicating that trialkylated products are likely to have been formed due to further alkylation as evidenced by GC analysis. The strong acidic strength of sulfuric acid may be the reason for multiple alkylated products formation. From the conversion and selectivity data, it may be derived that for the formation of monoalkylated resorcinol only weak acid sites are required. The formation of dialkylated product from the monoalkylated product is favored only when the steric hindrance is less, i.e. the catalysts should have large pores to allow the bulky alkylated products to travel out.

The selectivity of the 4,6-di-*tert*-butyl resorcinol is increased in the order HZSM-5 < HM < HY < acidified mont.-K10. It is likely that some dialkylated product are formed on the external surface of the zeolites, because 4,6-di-*tert*-butyl resorcinol is too large to penetrate into the zeolites channels. The selectivity of 4-*tert*-butyl resorcinol is more or less identical for the zeolites, HZSM-5, HY, HM even though the conversions of these zeolites vary due to differences in acidity.

The conversion and selectivity patterns of the alkylated products formed over zeolites and clay materials reveal that the temperature, acidity and pore-structure of the catalyst materials influence the reaction. Modified mont.-K10 is a very good candidature for *tert*-butylation of resorcinol, especially for producing dialkylated resorcinol and much superior over conventional sulfuric acid. Low temperature and weak acid sites seem to favor the monoalkylated resorcinol selectively even though the conversion is low. At high temperature, the conversion increases so does the dialkylated product. The strong acidity also favors dialkylation. It appears that the alkylation reaction proceeds via mono to dialkylation in a sequential fashion. The larger pore-size as in the case of modified mont.-K10 having wider interlamellar spacing compared to pristine clay also contribute to the dialkylation.

4. Conclusion

Several solid acid catalysts have been used for *tert.*-butylation of resorcinol. Modified mont.-K10 with wider pore-structure and required acidity seems to be a very good catalyst compared to HY, HZSM-5, HM, pristine mont.-K10 and even H_2SO_4 .

Acknowledgements

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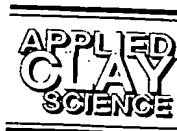
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Clays and catalysis: a promising future

A. Vaccari *

*Dipartimento di Chimica Industriale e dei Materiali, Università degli Studi di Bologna,
Viale del Risorgimento 4, 40136 Bologna, Italy*

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Abstract

The main properties of cationic and anionic clays as well as their role in catalysis are discussed in light of the versatility and potential of these materials. Clays exhibit specific features such as high versatility, wide range of preparation variables, use in catalytic amounts, ease of set-up and work-up, mild experimental conditions, gain in yield and/or selectivity, low cost, etc., which may be very useful tools in the move towards establishing environmentally friendly technologies. Furthermore, the possibility of upgrading these materials by the pillaring process opens new and interesting perspectives, also considering possible shape selective advantages. Recent catalytic applications of cationic and anionic clays in organic or fine chemistry (acid- or base-catalyzed reactions, Diels–Alder reactions, reactions using metallic nitrates, etc.), environmental catalysis (DeSOx, DeNOx or contaminant oxidation) and energy exploitation (partial oxidation of methane) are discussed as very promising research subjects with a wide range of possible future developments. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: smectites; hydrotalcites; pillared layered clays; heterogeneous catalysts; organic syntheses; environmental applications; methane activation

1. Introduction

Clays are very versatile materials and hundred of millions of tons currently find applications not only in ceramics and building materials, paper coatings and fillings, drilling muds, foundry moulds, pharmaceuticals, etc, but also as adsorbents, catalysts or catalyst supports, ion exchangers, etc, depending on their

* Tel.: +39-051-6443683; Fax: +39-051-6443680; E-mail: vacange@ms.fci.unibo.it

specific properties (Grim, 1968; Van Olphen and Fripiat, 1979; Nemezc, 1981; Fodwen et al., 1984; Reichle, 1986a; Newman, 1987; Decarreau, 1990; Schoonheydt, 1991; Cavani et al., 1991). Two broad classes of clays may be identified (Reichle, 1986a): cationic clays (or clay minerals), widespread in nature, and anionic clays [or layered double hydroxides (LDHs)], more rare in nature but relatively simple and inexpensive to synthesize on laboratory and industrial scales (Cavani et al., 1991; Trifirò and Vaccari, 1996). The cationic clays have negatively charged alumino-silicate layers, with small cations in the interlayer space to balance the charge, while the anionic clays have positively charged brucite-type metal hydroxide layers with balancing anions and water molecules located interstitially. Cationic clays are mainly prepared starting from the minerals (Grim, 1968; Van Olphen and Fripiat, 1979; Nemezc, 1981; Fodwen et al., 1984; Reichle, 1986a; Newman, 1987; Decarreau, 1990; Schoonheydt, 1991), whereas anionic clays are usually synthesized (Miyata, 1977, 1980; Reichle, 1986b; Cavani et al., 1991; de Roy et al., 1992; Vaccari, 1992; Trifirò and Vaccari, 1996).

Considering that environmental issues as well as process optimization require the substitution of liquid acids and bases by more friendly solid catalysts, cationic and anionic clays may be considered very promising substitutes, due to their high versatility, easily manipulated properties and/or wide range of preparation variables (mainly for anionic clays), low costs, etc. Promising applications appear continuously in the literature and further ones in new and unexpected areas can be looked forward to in the near future, especially taking into account the possibilities for technological upgrading of these materials, with the transition from 2- to 3-dimensional structures via the preparation of pillared clays.

In this contribution, the properties of cationic and anionic clays more relevant in catalysis are examined and recent catalytic applications in different fields of relevant scientific and industrial interest are discussed, with the goal of illustrating the flexibility of these materials and the wide range of their current and possible applications.

2. Cationic clays

2.1. *Main physical and chemical properties*

The main properties relevant for catalytic applications are affected considerably by the composition and particle size (Grim, 1968; Van Olphen and Fripiat, 1979; Bailey, 1980; Nemezc, 1981; Fodwen et al., 1984; Burch, 1987; Newman, 1987; Decarreau, 1990; Schoonheydt, 1991; Vaccari, 1998). For example, the BET surface area determined by N₂ adsorption decreases with increasing

particle size, evidencing that only the external surface area is accessible to nitrogen and, even less, to larger molecules. The experimental values ($50\text{--}150\text{ m}^2\text{ g}^{-1}$ ca.) are significantly lower than those calculated for single layer particles ($800\text{ m}^2\text{ g}^{-1}$ for $2\text{ }\mu\text{m}$ particles). Furthermore, the different surface areas determined as a function of drying procedure and, mainly, type of exchangeable cations, indicate that the number of layers per aggregate and the agglomeration of the aggregates in a powder are cation and drying-procedure dependent.

The cation exchange capacity (CEC) is also related to the particle size. The structural formulae give the amount of negative charge per unit cell due to isomorphous substitution (i.e., the pH-independent part). At the edges of the crystals the sheet structure is broken and terminated by OH-groups, that may contribute to the CEC. This contribution depends on the crystal size, pH and type of exchangeable cations and may reach, for example, 10% ca. of the total CEC for particles of 100 nm. Obviously, determination of the layer charge density (i.e., the CEC per unit of surface) is subject to the same difficulties of the CEC and surface area determinations, although a value of about $1\text{ e}^- \text{ nm}^{-2}$ has been reported as average for smectites (Kwon and Pinnavaia, 1989).

As a function of their small particle size, clays may exhibit both Brönsted and Lewis acid sites: the former are the external OH-groups, while the Lewis sites are the exposed or three-fold coordinated Al^{3+} ions, substituting for the Si^{4+} ions in the tetrahedral sheets. The strength of the Brönsted sites may be determined by Hammet indicators, butylamine titration or IR spectroscopy using probe molecules (Benesi and Winquest, 1978; Newman, 1987; Cornelis and Laszlo, 1990; Schoonheydt, 1991; Knozinger, 1993), with a direct correlation between acid strength and composition (Table 1). Recently, the synthesis of a clay superacid, with Hammett acidity ranging from -13.2 to -12.7 has also been reported (Li et al., 1995a,b). The number of acid sites titrated by butylamine is always lower than the CEC (0.98 meq g^{-1} for montmorillonite), showing that in apolar solvents the interlamellar space is not fully available for the reaction, although in the protonated montmorillonite partial destruction of the lattice cannot be excluded. Furthermore, the surface acidity decreases as the

Table 1

Acid strength and acidity (determined either by Hammett indicators in an aprotic solvent or by butylamine titration) of some clays (Benesi and Winquest, 1978; Newman, 1987; Schoonheydt, 1991)

Clay	H_0
Na^+ -montmorillonite (0.04 meq g^{-1})	$-3.0 < H_0 < +1.5$
NH_4^+ -montmorillonite	$-3.0 < H_0 < +1.5$
H^+ -montmorillonite (0.65 meq g^{-1})	$-8.2 < H_0 < -5.6$
Acid treated clay	< -8.2

amount of residual water in the clay increases, with an extension related to the nature of the exchangeable cations (Schoonheydt, 1991). On the other hand, many clays swell in liquid water with an increase in the distance between the elementary layers up to aggregate disintegration and transformation of the original suspension into a gel. Analogously, using polar solvents a significant increase in the interlamellar space accessible to organic substrates can be achieved.

Not only acid sites, but also electron-accepting or oxidizing sites may be located at the edges or in the structure. The former may be identified as trigonal Al^{3+} ions, acting as Lewis sites, while Fe^{3+} ions in the lattice are the structural oxidizing sites (Theng, 1974). Moreover, redox properties may be induced by the exchangeable cations, such as Cu^{2+} , Ag^+ , Fe^{3+} or Ru^{3+} (Soma et al., 1986a,b). Furthermore, the interaction of a solid surface with organic molecules depends on its hydrophobicity. A weak interaction precludes any catalytic step, while too strong clinging of organic products to the surface makes desorption too slow or impossible. Again, the hydrophilic/hydrophobic nature of the surface may be manipulated by an appropriate choice of the exchangeable cations (Cornelis and Laszlo, 1990).

A further key point to improve material design in the clays is the pillaring step, i.e., the synthesis of materials having 3-D network structures like that of zeolites. Indeed, the main goal of the pillaring process has been and continues to be that of producing new and inexpensive materials, with properties complementary to those of zeolites (pore size and shape, acidity and redox properties, etc.). Pillared layered clays (PILC's), nanocomposite materials with open and rigid structures are obtained by linking robust, three-dimensional species to a layered host. The final properties of PILC's can be modulated by carefully choosing the different parameters, such as nature of the pillaring agent, type of clay and particle size, pillaring procedure, thermal treatments, etc., thus offering a very powerful and flexible way to design tailored catalysts. Therefore, control of the pillaring process is a very promising means to obtain solids with i) very high surface areas (up to $600 \text{ m}^2 \text{ g}^{-1}$), ii) a broad spectrum of properties (structural, chemical, catalytic, etc.), and iii) controlled internal structures, with reactive sites and/or species chosen to match particular applications or provide host structures for chemical or physical processes.

It is evident that PILC's are so wide and important a subject as to require at least a full paper, however discussion here is limited to a brief summary of the main aspects. For more complete and detailed information, reference should be made to the original literature (e.g., Pinnavaia, 1983; Burch, 1987; Occelli et al., 1987; Figueras, 1988; Vaughan, 1988; Decarreau, 1990; Mitchell, 1990; Schoonheydt, 1991; Butruille and Pinnavaia, 1996). The pillaring process requires a clay with a relatively low negative charge density and a chemical substance with a large positive charge. For example, using highly charged vermiculites, the polyoxocations are not stable and may hydrolyze almost

completely. On the other hand, starting from a single clay, controlled calcination can be used to prepare a series of samples with CEC ranging from that of the raw material down to virtually zero (Burch, 1987; Purnell, 1992). Under the conditions that i) the guest species are homogeneously distributed, ii) the clay sheets are rigid and do not bend, iii) all the sheets are pillared, and iv) the adsorption of the pillaring molecules on the external surface is negligible, a two dimensional channel system is generated (unlike in zeolites in which three-dimensional channel systems are present).

Many different pillaring agents have been reported in the literature (organic compounds, metal trischelates, organometallic complexes, metal cluster cations, metal oxide sols, polyoxocations, etc.). Many of these species however have some drawbacks, such as low reactivity or lack of thermal stability. Polyoxocations are by far the most widely employed pillaring agent. Different polyoxocations (Al, Ni, Zr, Fe, Cr, Mg, Si, Bi, Be, B, Nb, Ta, Mo, Ti and more recently Cu and Ga) have been reported in the open and patent literature and clays with multielement pillars also have been prepared (Carrado et al., 1986; Occelli, 1986; Burch, 1987; Vaughan, 1987, 1988; Figueras, 1988; Decarreau, 1990; Mitchell, 1990; Schoonheydt, 1991). However, the chemical composition, structure and charge are well defined only for the Al-polyoxocation, in which the Keggin ion $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ is identified.

Preparation of PILC's consists in a controlled hydrolysis reaction which can be carried out in solution or in the interlamellar space of the clay (the former allows better control of the nature of the polyoxocations). In addition to the different parameters already mentioned, the calcination process also plays a key role. Three general cases may occur: i) the polyoxocations exit from the clay (no pillaring), ii) they degrade in situ giving rise to layers of aluminum hydroxide (1.4 nm thick, corresponding to a pseudo-chlorite), and iii) in the case of true pillaring, the polyoxocations dehydrate up to 573 K and dehydroxylate between 573 and 673 K. At higher temperatures, the pillars transform progressively, but the clays maintain the initial spacing of about 1.9 nm, while at $T > 1073\text{--}1173$ K the clays degrade. The stability of pillared clays as a function of the calcination temperature depends on the nature of the clays and the composition of the pillars. For example, an increase in stability may be achieved using mixed polyoxocations or by doping with small amounts of another element (Carrado et al., 1986; Occelli, 1986; Burch, 1987; Vaughan, 1987; Figueras, 1988; Decarreau, 1990; Mitchell, 1990; Schoonheydt, 1991; Purnell, 1992).

Cationic clays are mainly obtained from natural materials, that invariably contain impurities, although they can also be synthesized such as for example laponite® or optigel-SH® (analogs of hectorite, by Laporte Industries and Sud-Chemie, respectively). By means of centrifugation it is possible to obtain a $< 2\text{ }\mu\text{m}$ suspension of clay, while the precipitate mainly contains the impurities. Amorphous Fe- or Al-oxides may remain adsorbed on the clay particles, but the chemical treatments to remove them are not simple and present many problems

(Decarreau, 1990; Schoonheydt, 1991). However, from the viewpoint of making catalysts at a competitive price, three important criteria need to be met: i) use the whole clay material, after minimal refining (i.e., low cost), ii) pillar the Ca or (Ca, Na) forms, not only the Na forms (i.e., no pre-exchange), and iii) be able to use clay-polyoxocation concentrations ($> 15\%$ solids) that can be economically and effectively spray-dried to give a usable particle size distribution (40–200 μm) (Burch, 1987).

2.2. Catalytic applications

The first industrial application of clays as catalysts dates back to 1915. Acid treated smectites have been known for more than fifty years as catalysts for oil cracking (Houdry process), although after 1964 they were replaced by zeolites, due to their better activity and selectivity (Csicsery, 1984; Burch, 1987; Figueras, 1988; Decarreau, 1990). However, the most promising catalytic applications of natural and/or modified clays are in the field of organic and/or fine chemistry, showing specific features such as use in catalytic amounts (unlike AlCl_3), simple recovery and reuse of the catalyst, ease of set-up and work-up, mild experimental conditions, gains in yield and/or selectivity, etc. which may be very useful tools in the move towards establishing environmentally friendly technologies (Comelis and Laszlo, 1985, 1990, 1994; Laszlo, 1986; Vaccari, 1998). Furthermore, acid treated clays can also be used as supports for microwave-activated organic reactions in the absence of solvent (Brown, 1994). The high reactivity achieved is in part due to the stability of the clay supports towards intense microwave fields and further improvements may be possible with optimized acid-clay supports.

The acid treatment of clays may be performed either by simple washing with a mineral acid (i.e., exchanging the interlamellar cations with protons) or by heating for variable times a suspension of clay in a mineral acid (for example at 368 K with 30% H_2SO_4) (Rhodes and Brown, 1993, 1994). The optimum acid treatment conditions vary from one clay to another, depending on the chemical composition, level of hydration, nature of the exchangeable cations and, mainly, reaction conditions (see below). For example, in a recent paper (Sabu et al., 1993) it was reported that some natural Indian clays having Fe^{2+} and Ti^{2+} ions in their lattice showed, after a treatment for 45 min in boiling 2 M HCl, a catalytic activity in benzene alkylation significantly higher than those of the pure clay and of some reference materials (K10[®] or KSF[®] as well as some Lewis acids supported on K10[®]).

Commercial modified montmorillonites K10[®] or KSF[®] (by Sud-Chemie or Fluka Chemical) and F-13[®] or F-20[®] (by Engelhard), widely used industrially as acid catalysts or adsorbents in hydrocarbon cracking and, thus, well-defined and reliable materials, may be employed as reference materials. On the basis of the currently available literature, K10[®] is by far the most commercially

available acid-treated clay investigated. Clays or acid treated clays may also be effective supports for many inorganic salt catalysts or reagents, including Lewis acids (such as ZnCl_2 , AlCl_3 or FeCl_3) and Fe(III) or Cu(II) nitrates (Cornelis and Laszlo, 1985, 1990, 1994; Laszlo, 1986; Cornelis et al., 1990; Rhodes and Brown, 1993, 1994; Jang et al., 1995a,b). For example, *Clayzic*, *Kaozic* or *Japzic* are acronyms for K10[®]-, kaolinite- or Japanese acid clay-supported zinc chloride, respectively; analogously, *Clayfen* and *Claycop* are the acronyms for Fe(III) or Cu(II) nitrates supported on K10[®] clay and prepared in a similar way. Although commercially available acid-treated clays have most often been employed as supports for this type of catalyst/reagent, the structural requirements for the support vary widely and maximum activity generally requires 'tuning' of the support for individual adsorbed salts (Brown, 1994).

The acid treatment conditions corresponding to maximum catalytic activity depend on the precise reaction being catalyzed (Rhodes and Brown, 1994). Reactions between polar molecules require clays acid treated in mild conditions or for short times, capitalizing on the large number of acid sites available in the internal surface. In contrast, the surface accessible to apolar molecules consists only of the external face and edge areas of the clay platelets. These reactions require more severely treated clays and the catalytic activity depends on fine tuning of the changes in surface area and decrease in cation exchange capacity. In a swelling medium, optimum catalytic activity can be achieved not through acid treatments, but simply by ion exchange with acidic cations such as Al^{3+} ions. On the contrary, this last treatment has a negligible effect in a nonswelling medium (Elsen et al., 1995). In a recent paper (Vanden Eynde et al., 1995), K10[®] has also been applied in the formation under standard conditions of carbon–nitrogen bonds and, more generally, in the chemistry of nitrogen derivatives, coupling a catalytic activity similar to that, for example, of HCl to easy separation, low cost and possible recycle.

On the other hand, solid acid catalysts can also be employed in vapour phase syntheses, with evident advantages in comparison to the conventional liquid phase reactions due to more safe conditions, continuous production and ease of operation. For example, the synthesis of alkylquinolines has been recently reported using either zeolites (MCAater et al., 1997) or K10[®] montmorillonite (Campanati et al., 1997) as catalysts. In the latter case, 2-methyl-8-ethylquinoline (MEQUI) was synthesized from ethylene glycol and an excess of ethylaniline, the reaction being favoured by increasing the temperature and amount of ethylene glycol and operating in a partially reducing atmosphere (Table 2). A possible reaction pathway was proposed (Fig. 1), in which MEQUI is formed by cycloaddition, and successive dehydrogenation reactions, with the preliminary formation of crotonaldehyde as an intermediate (Campanati et al., 1997).

For supported Lewis acid catalysts the activity also depends on the nature of the organic substrate. For example, maximum activity in the Friedel–Crafts alkylation of benzene by benzyl chloride was found using a clay treated by acid

Table 2

Catalytic data as a function of the feedstock and reaction conditions employed in the vapour phase synthesis of MEQUI, using K-10[®] as catalyst (Campanati et al., 1997)

Reaction temperature (K)	Gas mixture	GHSV (h ⁻¹)	LHSV (h ⁻¹)	Yield (%)
603	N ₂	3000	0.1 ^b	25
563	N ₂	3000	0.1 ^b	18
523	N ₂	3000	0.1 ^b	11
563	N ₂	3000	0.1 ^c	26
563	N ₂	900	0.1 ^b	11
563	N ₂	180	0.1 ^b	12
563	N ₂	900	0.2 ^c	27
603	N ₂	3000	0.1 ^d	33
603	N ₂	3000	0.1 ^e	41
603	H ₂ /N ₂ = 1:9 (v/v)	3000	0.1 ^b	31
603	H ₂ /N ₂ = 1:9 (v/v)	3000	0.1 ^f	29

^aIn order to take into account the carbon number in the feed, the yield in MEQUI was calculated according to: A) moles of MEQUI obtained/0.5 moles of ethylene glycol fed × 100; B) moles of MEQUI obtained/moles of crotonaldehyde fed × 100.

^b2-ethylaniline/ethylene glycol (10.0:1.0 mol/mol).

^c2-ethylaniline/ethylene glycol/water (10.0:1.0:0.1 mol/mol).

^d2-ethylaniline/ethylene glycol (5.0:1.0 mol/mol).

^e2-ethylaniline/ethylene glycol (1.0:2.0 mol/mol).

^f2-ethylaniline/crotonaldehyde (10.0:0.5 mol/mol).

for a long time (20 h) as the support. This support had almost no clay features, a relatively low surface area and mesopores (10–14 nm range), in which the active fraction of ZnCl₂ was adsorbed (Elsen et al., 1995). On the contrary, with anisole, optimum activity was achieved using supports treated for short times, with evidence of a significant contribution by the Brønsted acid sites on the clays. This result together with the low activity of the catalyst, suggests that ZnCl₂ Lewis acid sites are quite strongly coordinated by anisole, reducing their catalytic activity (Elsen et al., 1995). However, a quantitative yield for this reaction after 15 min at room temperature using K10[®] impregnated with ZnCl₂ (*Clayzic*) also has been reported (Clark et al., 1989).

Friedel–Crafts acylations may be effectively catalyzed by clays modified through exchange of the interlamellar cations or impregnation of metal chlorides (Cornelis et al., 1990). A comparison of the catalytic performances in the benzylation of mesitylene (Table 3) and anisole showed the superior performances of the exchanged clays in comparison to those of the impregnated clays (Cornelis et al., 1990). In the impregnated clays, the catalytic activity depends more on the activation procedure adopted than the nature of the starting clay. Furthermore, the authors reported for the exchanged clays a strong dependence on the type of reaction and nature of the reaction partners, with, for example, an

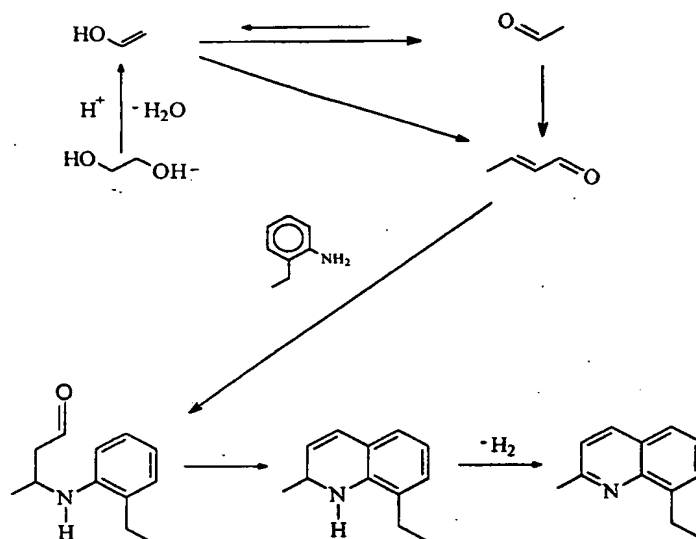


Fig. 1. Reaction pathway for the vapour phase synthesis of 2-methyl-8-ethylquinoline from 2-ethylaniline and ethylene glycol, using K-10[®] as catalyst (Campanati et al., 1997).

efficiency scale in the acylation of *p*-xylene by benzoyl chloride ($\text{Zr}^{4+} < \text{Ti}^{4+} < \text{Al}^{3+} < \text{Cu}^{2+} < \text{Cr}^{3+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Fe}^{3+}$) totally different from the sequence of bulk metallic chlorides in Friedel–Crafts reactions (Laszlo and Mathy, 1987;

Table 3

Benzoylation of mesitylene by benzoyl chloride using either impregnated or exchanged catalysts (Cornelis et al., 1990)

Catalyst	Reaction temp. (K)	Reaction time (min)	Yield (%)
Kaozic-533 ^a	343	1800	85
Japzic-533	343	1800	72
Kaozic-533	433	60	74
Japzic-533	433	60	100
Japzic-673	433	15	100
Clayzic-533	433	10	100
K10 [®] -Al ³⁺	433	15	98
K10 [®] -Ti ⁴⁺	433	15	100
K10 [®] -Cr ³⁺	433	15	94
K10 [®] -Fe ³⁺	433	15	98
K10 [®] -Co ²⁺	433	15	100
K10 [®] -Cu ²⁺	433	15	84
K10 [®] -Zn ²⁺	433	15	85

^aActivation temperature (K).

Olah, 1992). On the other hand, the nature of the acylating agent must also be considered. For example, with mesitylene using different acyl chlorides, the yields in the acylation product depended on both the activity and the stability of the electrophilic species RCO^+ previously formed (Fig. 2) (Campanati et al., 1998). However, similar data were obtained using acetyl chloride or anhydride, with evident advantages in comparison to the homogeneous reaction catalyzed by AlCl_3 (Fig. 3).

Cornelis and Laszlo (1994), stressing the advantages of Friedel–Crafts clay catalysts (high substrate selectivity, improved yields, conversions, and reaction times, and reduction in the amount of catalyst by up to a factor of 2000), claimed that their scientific work was the basis of the development of a commercial line of catalysts (Envirocats[®], Contract Chemicals). Clays or acid treated clays can also be useful supports for elements other than transition ions. Many other elements have been investigated for the preparation of catalysts or supported reagents, for example, Pt, Pd, Ru, Rh, Ni, or Cu to produce hydrogenation catalysts, in which the lamellar structure of the support may confer useful size and shape selectivity (Brown, 1994).

Another promising application of clay catalysts is in Diels–Alders reactions. Kaolinites catalyze effectively the normal electron-demand Diels–Alder cy-

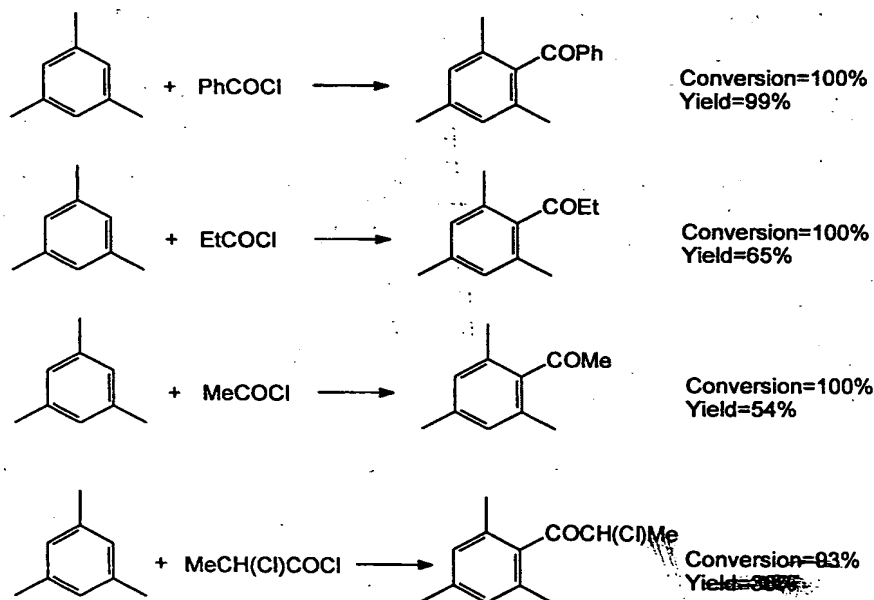


Fig. 2. Role of the nature of the acyl chloride in the reaction with mesitylene (catalyst = K-10[®], reaction temperature = 473 K, reaction time = 15 min). Conversion referred to the acyl chloride (Campanati et al., 1998).

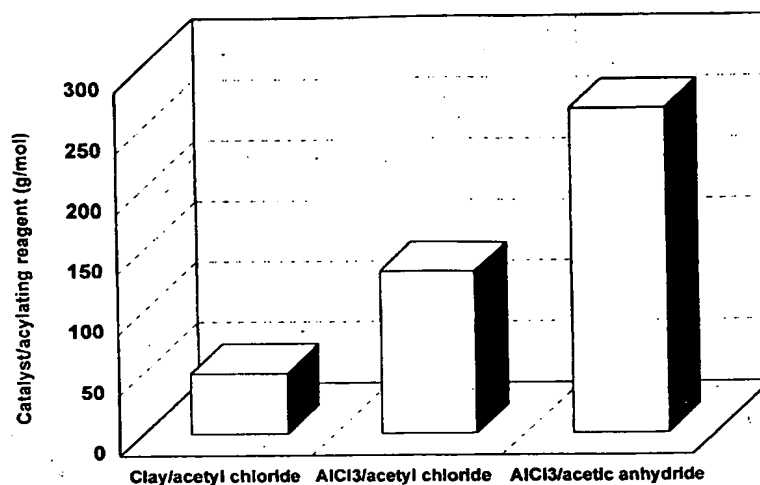


Fig. 3. Ratios between the amounts of catalyst and acetyl chloride or anhydride in the acylation of mesitylene using homogeneous or heterogeneous catalysts [for the latter the same values were obtained with both acylating reagents (Campanati et al., 1998)].

clodaddition, presumably through stabilization of the dienophile by hydrogen bonding, thus reducing the HOMO (diene)–LUMO (dienophile) energy gap. The stereoselectivity, i.e., the endo preference is rather high, provided that humidity be carefully excluded from the reaction medium to avoid irreversible deactivation (Cornelis and Laszlo, 1994). On the contrary, by choosing a clay mineral with high layer charge, and thus narrower interlamellar space, the proportion of the kinetically less favoured, but less bulky, *exo* isomer may be improved (Fig. 4) (Adams et al., 1994).

The applications of clays or modified clays are not limited to use as catalysts. Many other interesting examples have been reported in the literature on their use as supported reagents (Cornelis and Laszlo, 1985, 1990, 1994; Laszlo, 1986; Brown, 1994), although nowadays only on a laboratory scale. For example, the nitration of phenols, that normally is performed using mixtures of nitric and

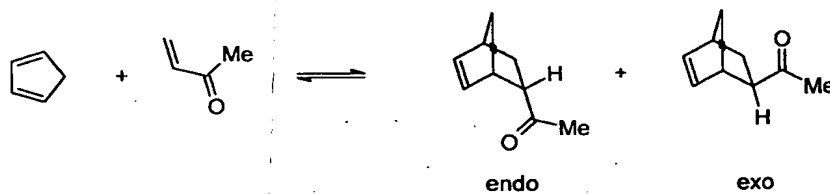


Fig. 4. Synthesis of *exo*- and *endo*-isomers by Diels–Alder reaction between cyclopentadiene and methylvinylketone (Adams et al., 1994).

sulphuric acids, with only modest overall yields (60% ca.) and formation, together with the normal *ortho*- and *para*-substituted derivatives, of the meta isomer and by-products of polynitration. The clay-supported ferric nitrate (*Clayfen*) not only improves significantly the overall yield in the nitration of phenol (up to 90% ca), but is also very active in the nitration of many other phenols with a high regioselectivity (Table 4), nearly ruling out both formation of the meta isomer and hazardous polynitration (Cornelis and Laszlo, 1985, 1994; Brown, 1994). For estron nitration (an important process in the pharmaceutical industry as the gateway to various estrogenic drugs) the yield obtained is a significant improvement over the best value previously reported (39%), decreasing the cost per gram of the target molecule by about a factor of 3 (Cornelis and Laszlo, 1994).

Another promising field of application is that of certain organic clays as triphase catalysts in nucleophilic displacement reactions. For example the methyltriocrylammonium exchanged form of hectorite (exhibiting a basal spacing corresponding to a lateral bilayer structure) gives very high yields over a wide range of nucleophiles (Table 5) (Pinnavaia, 1995). Furthermore, this type of material makes it possible to overcome the environmental problems related to the use of free quaternary onium ions as phase transfers or due to the low accessibility or stability of onium ions supported on polymers or oxides (Regen, 1976; Tundo et al., 1982).

In concluding, it should be emphasized that the use in organic syntheses of clay or clay-modified catalysts or reagents commends itself by its simple implementation, the small amount of catalyst required (in comparison to standard Lewis acids, such as AlCl_3) and the use of more environmentally compatible conditions and/or substances, for instance metal salts trapped between the layers of a commercial and inexpensive clay. Furthermore, clay microreactors may display enzyme-like characteristics.

Table 4
Yield (%) at room temperature in the nitration of various phenols using clay-supported ferric nitrate (*Clayfen*) (Cornelis and Laszlo, 1985; Laszlo, 1986; Cornelis and Laszlo, 1994)

Phenol	Ortho (%)	Para (%)	Reaction conditions
—	39	41	Ether, 20 h
4-CH ₃	58	—	Ether, 20 h
3-CH ₃	20	34	Ether, 20 h
4-Cl	88	—	Ether, 20 h
4-F	69	—	Ether, 20 h
β -naphthol	63	—	Toluene, 5 h
4- <i>t</i> -C ₄ H ₉	92	—	Tetrahydrofuran, 2 h
3-OH	58	—	Toluene, 1.5 h
4-CHO	93	—	Ether, 2 h
Estrone	55	—	Toluene, 72 h
			Toluene, 24 h

Table 5

Triphase nucleophilic displacement reactions carried out in the presence of $[(n\text{-C}_8\text{H}_{17})_3\text{NMe}]^+\text{-hectorite}$ (Pinnavaia, 1995)

Substrate	Nucleophilic reagent	Substrate to Onium ion (mol/mol)	Time (h)/temperature (K)	Product	Yield (%)
$n\text{-C}_5\text{H}_{11}\text{Br}$	$\text{C}_6\text{H}_5\text{OH}$ (2.5 mol)/ 2.5 M NaOH	100	1.5/363	$n\text{-C}_5\text{H}_{11}\text{OC}_6\text{H}_5$	83
$n\text{-C}_5\text{H}_{11}\text{Br}$	NaSCN (10 mol)	200	1.5/363	$n\text{-C}_5\text{H}_{11}\text{SCN}$	99
$n\text{-C}_5\text{H}_{11}\text{Br}$	NaS (6 mol)	100	0.5/363	$(n\text{-C}_5\text{H}_{11})_2\text{S}$	91
$n\text{-C}_5\text{H}_{11}\text{Br}$	$\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ (19 mol)/ 50% NaOH	100	65/323	$(n\text{-C}_5\text{H}_{11})\text{CH}(\text{CN})\text{C}_6\text{H}_5$	86
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	10% NaOCl (7 mol)	40	10/323	$\text{C}_6\text{H}_5\text{CHO}$	83

Coming now to PILC's, they are generally less active than starting clays in reactions conducted up to 523 K, although it may be relatively simple to regenerate activity (Burch, 1987; Decarreau, 1990; Schoonheydt, 1991; Purnell, 1992). It is in the area of reactions at high temperature that PILC's have been investigated the most, mainly for typical reactions of interest to the refining industry, due to their specific properties (thermal and/or hydrothermal stability, selectivity, low cost, etc.). These applications have been thoroughly reviewed in previous papers (e.g., Burch, 1987; Figueras, 1988; Decarreau, 1990; Mitchell, 1990), I should like here only to emphasize, for example, that the progress in FCC in recent years has been rapid and dramatic, requiring a continuous increase in the maximum temperature of hydrothermal stability and, consequently, changing the target of PILC research (Burch, 1987). In concluding this brief survey, two applications can be cited, which in my opinion appear to be very promising: the reactions on bulky organic substrates and the SCR of NO. Again, important examples of the first class of reactions can be found in the references cited (Burch, 1987; Figueras, 1988; Mitchell, 1990; Elsen et al., 1995). Unlike clays, PILC's have a rigid structure and no differences are observed as a function of the reaction medium. Furthermore, the pore size of a PILC, which plays an important role in shape-selective catalysis, is determined both by interlayer distance and by lateral distance or pillar density. The interlayer distance depends on the size of the pillaring species, while the lateral distance is regulated by the charge density of the clay and by the extent of the pillaring process (Burch, 1987). Pillared clays exhibit broader pore size distributions than zeolites, which can be controlled and adjusted to a desirable predominant size (Schoonheydt, 1991; Butruille and Pinnavaia, 1996). Although PILC's are generally defined as having at least 50% of their surface area in pores less than 3.0 nm (Burch, 1987), narrower ranges have been reported by many authors (e.g., Burch, 1987; Figueras, 1988; Schoonheydt, 1991; Safdar Baksh et al.,

1992; Butruille and Pinnavaia, 1996; Tanev et al., 1998). It is therefore possible to use PILC's in the reactions of bulky organic molecules. Among these applications, of particular industrial relevance is the synthesis of durene, raw material to produce pyromellitic anhydride and, from it heat-resisting polymers (Kikuki et al., 1985; Matsuda et al., 1986).

Different PILC's (containing Zr, Cr, Fe, Al or Ti) have recently been investigated and claimed as a promising new class of catalysts for SCR of NO by NH_3 , with activity higher than that of commercial V_2O_5 -based catalysts (Yang et al., 1992). In particular, a superior poisoning resistance was claimed related to the possibility of forming PILC catalysts having a bimodal pore structure, where the macropores in the interparticle spaces act as feeder pores to micropores and act as filters, whereas the intraparticle micropores containing the active species carry out the catalytic action in the SCR reaction without any inhibition by the poisoning agents. del Castillo et al. (1986) confirmed the high activity of Ti-pillared clays and showed their high resistance to the presence of SO_2 . Finally, in a recent paper (Perathoner and Vaccari, 1997) an Al-PILC (AZA) and a mixed Al/Fe-PILC (FAZA), used as references by Concerted European Action—Pillared Layered Structures, were shown to be useful supports for Cu^{2+} ions to produce catalysts active in the SCR reaction. By comparison with other Cu-containing catalysts, (Fig. 5), it was shown that the mixed Fe/Al PILC exchanged with copper ions ($\text{CuO} = 3$ wt.%), allowed operation in a wider range of reaction temperatures, due to the reduced rate of

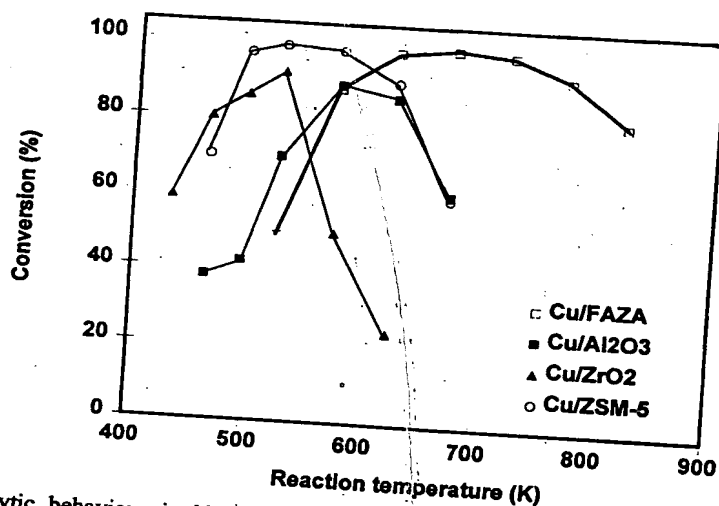


Fig. 5. Catalytic behaviour in NO reduction with NH_3 and O_2 of Cu/FAZA, Cu/ZSM-5 ($\text{CuO} = 3$ wt.%, prepared by ion exchange), Cu/ Al_2O_3 and Cu/ ZrO_2 ($\text{CuO} = 3$ wt.%, prepared by incipient wetness impregnation). Experimental conditions: atmospheric; pressure, NO = 1000 ppm, $\text{NH}_3 = 1250$ ppm, $\text{O}_2 = 35,000$ ppm and the remainder He; GHSV = $30,000 \text{ h}^{-1}$ (Perathoner and Vaccari, 1997).

side ammonia combustion. This is of particular interest in industrial applications where any temperature reduction of the flue gases has to be avoided. In the same paper a detailed FTIR investigation of the surface acidity, using different probe molecules was also reported in order to interpret the above effects.

3. Anionic clays

3.1. Main physical and chemical properties

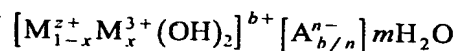
Anionic clays are natural or synthetic lamellar mixed hydroxides with inter-layer spaces containing exchangeable anions (Miyata, 1977, 1980; Reichle, 1986a,b; Cavani et al., 1991; Vaccari, 1992, 1998; de Roy et al., 1992; Trifirò and Vaccari, 1996), and many names are used depending on the composition and polytype form (Table 6) (Drits et al., 1987). The general terms hydrotalcite-type (HT) compounds or LDHs also are widely used. The former is probably due to the fact that extensive characterizations have been carried out on hydrotalcite (a Mg/Al hydroxycarbonate) which is easy and inexpensive to synthesize. On the other hand, the reference name LDH is derived from early works of Feitknecht, who hypothesized a structure with intercalated hydroxide layers (Feitknecht, 1942a,b). This hypothesis was refuted many years later on the basis of single crystal XRD analysis (Allmann, 1968; Taylor, 1969), which showed that all the cations are localized in the same layer, with the anions and water molecules located in the interlayer region. However, the terms HT compounds or anionic clays are not generally accepted, considering that the term refers strictly to a specific mineral and that these compounds do not fulfil some clay requirements, for example the very small particle size.

Anionic clays may be defined by their chemical composition, basal spacing

Table 6
Composition, crystallographic parameters and symmetry for some HT anionic clays (Drits et al., 1987)

Mineral	Chemical composition	<i>a</i> (nm)	<i>c</i> (nm)	Symmetry
Hydrotalcite	Mg ₆ Al ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.3054	2.281	3R
Manasseite	Mg ₆ Al ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.310	1.56	2H
Pyroaurite	Mg ₆ Fe ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.3109	2.341	3R
Sjögrenite	Mg ₆ Fe ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.3113	1.561	2H
Stichtite	Mg ₆ Cr ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.310	2.34	3R
Barbertonite	Mg ₆ Cr ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.310	1.56	2H
Takovite	Ni ₆ Al ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.3025	2.259	3R
Reevesite	Ni ₆ Fe ₂ (OH) ₁₆ CO ₃ ·4H ₂ O	0.3081	2.305	3R
Meixnerite	Mg ₆ Al ₂ (OH) ₁₆ (OH) ₂ ·4H ₂ O	0.3046	2.292	3R
Coalingite	Mg ₁₀ Fe ₂ (OH) ₂₄ CO ₃ ·2H ₂ O	0.312	3.75	3R

and stacking sequence. The general formula to describe the chemical composition is



where M = metal, A = interlayer anion, and $b = x$ or $2x - 1$, for $z = 2$ or 1 , respectively. Anionic clays have structures similar to that of brucite $\text{Mg}(\text{OH})_2$, and crystallize in a layer-type lattice as a consequence of the presence of relatively small twofold positively charged cations in close proximity to the non-spherical and highly polarizable OH^- ions (Oswald and Asper, 1977). If some Mg^{2+} ions are replaced isomorphously by cations with higher charge, but similar radius (Shannon, 1976), the brucite-type sheets become positively charged and the electrical neutrality is maintained by anions located in disordered interlayer domains containing water molecules.

The structures of anionic clays can accommodate a wide range of variables (nature and ratio of the cations, type and charge of balancing anions, amount of interlayer water, crystal morphology and size). Only a few of these variations appear in nature however and for instance, carbonate is the anion preferred (Miyata, 1977, 1980; Reichle, 1986a,b; Drits et al., 1987; Cavani et al., 1991; Vaccari, 1992, 1998; de Roy et al., 1992; Trifirò and Vaccari, 1996). On the contrary, a very high number of variables has been reported for synthetic clays (Table 7), which make it possible to produce tailor-made materials able to fulfil specific requirements. For example, in the literature anionic clays are reported containing Li^+ ions (Serna et al., 1982), the highly unstable V^{3+} ions (Rives et al., 1993) or noble metal ions (such as Ru, Rh, Pd or Ir) (Blom and Derouane, 1991; Bhattacharyya et al., 1995; Basile et al., 1996a; Basini et al., 1996), as well as a very wide range of possible anions: inorganic and organic anions, iso and heteropolyanions, complex anions and metallorganic complexes (Cavani et al., 1991; de Roy et al., 1992; Trifirò and Vaccari, 1996). There is practically no limitation to the nature of the anions, which only have not to form strong complexes with the cation present. The only problems are the preparation of compounds with anions different from carbonates (due to the difficulty of

Table 7

Factors influencing the synthesis of HT anionic clays (Miyata, 1977; Reichle, 1986b; Cavani et al., 1991; Vaccari, 1992, 1998; de Roy et al., 1992; Trifirò and Vaccari, 1996)

Structural variables	Preparation variables
Cation size	pH
Value of x [i.e., the $\text{M}^{3+}/(\text{M}^{3+} + \text{M}^{2+})$ ratio]	Precipitation method
Cation stereochemistry	Precipitation temperature
Cation mixture (nature and ratio)	Reagent concentration
Nature of balancing anions	Aging
Amount of interlayer water	Washing and drying
Crystal morphology and size	Presence of impurities

avoiding any contamination from CO_2) and the instability of the anions in the pH range in which the synthesis of the relative HT compounds occurs such as may occur with the Keggin-like heteropolyanions (Pope, 1983).

Divalent or trivalent cations having an ionic radius similar to that of Mg^{2+} ions (Shannon, 1976) may be accommodated in the octahedral sites in the brucite-type sheets and form anionic clays. However, even though Cu^{2+} ions have a suitable ionic radius, they precipitate preferentially as malachite-like phases, because of the Jahn–Teller effect, which for d^9 ions favours the formation of distorted octahedral structures (West, 1990). Other cations (e.g., Mg^{2+} , Co^{2+} or Zn^{2+}), which can form regular octahedral structures, favour the entrance of Cu^{2+} ions into ternary phases, which are obtained without side phases for $\text{Cu}^{2+}/\text{M}^{2+}$ ratios near to one (Busetto et al., 1984; Gusi et al., 1987). Notwithstanding the claims that HT compounds form for x values in the general formula in the range 0.1–0.5 (Thevenot et al., 1989), there are many indications that pure phases may form only for a narrow range ($0.20 < x < 0.34$). In many cases the side phases are amorphous, therefore not detectable by XRD, but only by other techniques such as thermogravimetric, electron microscopy or solid state ^{27}Al MASNMR analyses (Cavani et al., 1991; Trifirò and Vaccari, 1996).

Water molecules and anions are located in the interlayer space, and structural and physical properties indicate the strongly disordered nature of these regions, for which a quasi liquid state has been claimed (Allmann, 1968; de Roy et al., 1992). The interlayer space can also be used to increase the total amount of metals, which may be introduced in anionic form (chromates, ferro or ferricyanides, etc.), or to introduce cations which are not compatible with the octahedral sites of the brucite-type sheets (for example Mo^{4+} or Ir^{4+}), thus preparing new materials with unusual properties (Itaya et al., 1987).

As previously reported, anionic clays exhibit particle sizes higher than those claimed for clay minerals and this is reflected by the surface area values, that for the dried precipitates are generally lower than $100 \text{ m}^2 \text{ g}^{-1}$. Analogously to that previously shown for cationic clays, it is evident that these values refer only to the external area, and this may be even better understood considering the higher charge density of anionic clays (4 instead of $1 \text{ e}^- \text{ nm}^{-2}$) (Kwon and Pinnavaia, 1989). This high charge density creates strong electrostatic forces between the brucite-type sheets and the anions, thus swelling is much more difficult and has been reported using glycerol to produce HT compounds containing long-chain organic acids from meixnerite (Chibwe and Jones, 1989; Dimotakis and Pinnavaia, 1990).

Although the true exchange capacity of anionic clays [$1.0\text{--}1.5 \text{ meq g}^{-1}$ (Reichle, 1986a)] is usually much less than the theoretical one [3.3 meq g^{-1} for hydrotalcite (Bish, 1980; Tsuji et al., 1992)], they show a resistance towards temperatures higher than those of anion exchange resins and thus are used in some high temperature applications, such as treatment of the cooling water of

nuclear reactors (Miyata, 1985). The selectivity in the exchange increases with increasing anion charge density (Miyata, 1983; Yamaoka et al., 1989), i.e., anionic clays strongly prefer multiply charged anions and compounds containing nitrates or chlorides have to be indicated as the best precursors for exchange reactions. Moreover, very important is the pH of the solution, which may favour or prevent the exchange (Bish, 1980) and has to be compatible with both the range of stability of the starting anionic clay and the anion.

Anionic clays exhibit generally poor basic properties, sensibly lower than those of the mixed oxides obtained by their thermal decomposition (Miyata et al., 1971a,b; Reichle, 1986b; Cavani et al., 1991; Vaccari, 1992; Trifirò and Vaccari, 1996); however, very good basic properties have been recently claimed for meixnerite in the selective aldolisation of acetone (Tessier et al., 1995). Furthermore, Costantino and Pinnavaia (1994) have shown that thermal activation below the structural decomposition point (≤ 523 K) afforded catalysts with specific activities approximately an order of magnitude larger than the mixed oxides or MgAl_2O_4 spinel–MgO mixtures formed by calcination at 723 K and 1163 K, respectively. The authors hypothesized that adsorbed water can inhibit access to the basic sites on the surface of anionic clays; however, the nature and strength of the basic sites in dried precipitates have not been fully clarified. Moreover, basic properties depend also on composition, for example Zn/Al, Zn/Cr or Ni/Al anionic clays are less basic than Mg/Al clay (Kwon and Pinnavaia, 1989; Cavani et al., 1991).

There is a very interesting range between the decomposition temperature of an anionic clay and that of formation of stoichiometric spinels, in which metastable, generally poorly crystallized phases form. These phases have been referred to in the literature with many different names (NaCl-type mixed oxides, spinel-type phases or simply mixed oxides or mixed oxide solid solutions), however all authors agree that these mixed oxides have disordered structures, containing an excess of divalent cations in comparison to the amount present in stoichiometric spinels (Reichle, 1986b; Cavani et al., 1991; Vaccari, 1992; Trifirò and Vaccari, 1996). SEM analysis of these phases shows a retention of the original morphology, suggesting that during thermal decomposition steam and carbon dioxide escape through holes in the surface, without extensive change in the crystal morphology nor dealumination of the brucite-type sheets (Reichle et al., 1986; Trifirò et al., 1988). In agreement with this mechanism, initially the surface area increases considerably (2–3 times), then a further increase in temperature and formation of the stoichiometric spinel give rise to a dramatic decrease in the surface area. The most interesting properties of these mixed oxides may be summarized as follows (Cavani et al., 1991; Vaccari, 1992, 1998; Trifirò and Vaccari, 1996):

A) *High surface area* (100–300 m^2/g)

B) *Homogeneous interdispersion* of the elements thermally stable also in reducing conditions, with formation of very small stable metal crystallites.

C) *Synergetic effects* between the elements; due to the intimate interdispersion, which favours, for example, the development of unusual basic or hydrogenating properties. Basic properties depend significantly on composition and calcination temperature.

D) *Memory effect*, which allows reconstruction under mild conditions of the original structure by contact with solutions containing various anions.

To prepare pillared layered anionic clays (PILAC's) large, highly charged anions are required, because the charge in the interlayer space must be negative (Woltermann, 1984; Cavalcanti et al., 1987; Kwon et al., 1988; Twu and Dutta, 1989; Doeuff et al., 1989; Serwicka et al., 1997). Large anions impart large expansion of the interlayers, while a high charge decreases the interlayer population, thus providing access to the interlayer surface for other guest-species (Cavani et al., 1991; Trifirò and Vaccari, 1996). Even though many different anions have been claimed as pillaring agents [for example organic anions (Drezdon, 1988; Meyn et al., 1990; de Roy et al., 1992; Carlino and Hudson, 1994; Tagaya et al., 1994; Putyera et al., 1995; Costantino et al., 1997, 1998; Morioka et al., 1998), metalloporphyrins or metal complexes (Dutta and Puri, 1989; Sato et al., 1990; Pérez-Bernal et al., 1991; Carrado et al., 1993; Cervilla et al., 1994a,b; Bonnet et al., 1995, 1996; Chibwe et al., 1996)], only the increases in basal spacing have been reported, without any data on the surface area and porosity, i.e., on the presence of accessible space in the interlayer regions. Clearly, this does not mean that these compounds are less interesting from the scientific and industrial points of view, but the use of different terms (for example intercalated) would be more suitable to avoid misunderstandings (Trifirò and Vaccari, 1996).

PILAC's may be classified, for example on the basis of the type of pillaring anion present: i) isopolyanions (or isopolyoxometalates); ii) heteropolyanions (or heteropolyoxometalates) with a Keggin structure; and iii) ferro or ferricyanides. Notwithstanding the low negative charge (see below), anionic clays containing ferro or ferricyanides also may be considered as pillared clays, since the requirements of an increase in d spacing, surface area and interlayer accessibility are fulfilled (Table 8). PILAC's are not simple to prepare for the following reasons.

1) Exchange in anionic clays is more difficult than in smectite-like clays, because of the higher charge density or number of charges per unit of surface area. This creates strong electrostatic forces between the brucite-type sheets and the anions, with consequent 'stuffing' of the interlayers by the anions themselves when their charge is in the range -1 to -3 (Doeuff et al., 1989; Kwon and Pinnavaia, 1989).

2) Hydrolysis of the pillaring anions can be caused by the anionic clays, as a function of the nature of the cations present in the brucite-type sheets.

3) Anionic clays may decompose in the synthesis conditions, chosen on the basis of the stability of the pillaring agents.

Table 8

Values of d_{001} spacing and surface area for some pillared HT anionic clays (PILAC's) (Woltermann, 1984; Cavalcanti et al., 1987; Kwon et al., 1988; Twu and Dutta, 1989; Doeuff et al., 1989; Cavani et al., 1991; Trifirò and Vaccari, 1996)

HT anionic clay	Pillaring agent	d_{001} spacing (nm)	Surface area ($\text{m}^2 \text{g}^{-1}$)
Zn/Al	$\text{V}_{10}\text{O}_{28}^{6-}$	1.19–1.23	169
Li/Al	$\text{V}_4\text{O}_{12}^{4-}$	0.95	n.d.
Mg/Al	$\text{Mo}_7\text{O}_{26}^{6-}$	1.22	71
Zn/Al	$\alpha\text{-(H}_2\text{W}_{12}\text{O}_{40})^{6-}$	1.46	63
Zn/Al	$\alpha\text{-(SiV}_3\text{W}_9\text{O}_{40})^{7-}$	1.46	155
Mg/Al	$\text{PV}_3\text{W}_9\text{O}_{40}^{9-}$	1.20	136
Mg/Al	Fe(CN)_6^{4-}	1.10	246
Mg/Al	Fe(CN)_6^{3-}	1.10	235

4) Carbonates compete with the pillaring anions, readily giving rise to mixed phases, due to their high affinity with the positively charged cationic sheets.

5) The anionic clay structure is stable only at relatively low temperatures.

All the above factors restrict the choice of the starting anionic clays, the pillaring agent, the preparation conditions and field of application.

Anionic clays may be synthesized by various techniques. This does not mean that it is easy to prepare pure compounds, but only that different methods may be adopted as a function of the composition required. Considering the different methods of preparation [precipitation at constant pH (also called coprecipitation to indicate that all cations precipitate simultaneously, in a ratio fixed by the starting solutions), precipitation at variable pH, deposition/precipitation reactions, hydrothermal synthesis, anion exchange, structure reconstruction, two powder synthesis, electrochemical methods, hydrolysis reaction] (Cavani et al., 1991; de Roy et al., 1992; Trifirò and Vaccari, 1996; Martin et al., 1998a,b), it is evident that coprecipitation is the most useful method to prepare large amounts of anionic clays. However, in some cases true coprecipitation conditions may not be required, taking into account that i) the presence in a mixture smooths the differences in the precipitation pH of the single cations, ii) aging and/or hydrothermal treatments may rectify improper precipitation conditions through dissolution/coprecipitation reactions, and iii) in some cases pure anionic clays may not be required or the presence of other species may have beneficial effects (Gusi et al., 1985).

Together with the structural factors, other parameters have been claimed as important in the precipitation of anionic clays (Table 7). However some of them are of limited importance, for example unlike that reported in the literature (Imperial Chemical Industries, 1963; Doesburg et al., 1987; Thevenot et al., 1989; de Roy et al., 1992) in our preparations we have not observed any effect of the temperature and no aging procedure was necessary. In contrast, heating

Cu-containing precipitates as slurry caused partial destruction of the HT structure with formation of malachite-type phases (Busetto et al., 1984). On the contrary, very important is the pH at which the precipitation occurs as well as the method of pH variation, which may modify both the nature and properties of the solids obtained (Trifirò et al., 1988; Cavani et al., 1991; Trifirò and Vaccari, 1996). On the basis of the values of precipitation pH of the single hydroxides (Cavani et al., 1991; de Roy et al., 1992; Trifirò and Vaccari, 1996), a pH range of 8–10 may be generally indicated as optimum to prepare most anionic clays.

High pH values give rise to the dissolution of aluminum and some other ions, and also phase segregation may be favoured, as with Cu^{2+} ions forming CuO (Imperial Chemical Industries, 1963). At low pH the synthesis proceeds by a more complex pathway and is not complete, as indicated by the differences between the chemical composition of the phases obtained and that of the starting solutions (de Roy et al., 1992). Furthermore, the precipitation pH determines the crystallinity of the Cr-containing precipitates, probably because of the tendency of Cr^{3+} ions to form oligomer complexes (West, 1990; Clause et al., 1991).

Coprecipitation may be carried out at low or high supersaturation; the former is the method most frequently used and requires controlled experimental devices (Courthy and Marcilly, 1983; Cavani et al., 1991; Vaccari, 1992, 1998; de Roy et al., 1992; Trifirò and Vaccari, 1996). Anionic clays with anions other than carbonate may be prepared by precipitation under nitrogen using alkali hydroxides; however, small amounts of carbonates are always present (Miyata, 1975). Coprecipitation at high supersaturation gives rise to less crystalline materials, owing to the high number of crystallization nuclei (Clause et al., 1991). The precipitation may be carried out using the same devices reported above, by increasing the concentrations of the solutions and/or the addition rate, or by putting a solution of the salts of the elements into a solution containing a small excess of alkali bicarbonates or bicarbonate/carbonate mixtures, previously heated at 333 K (Gherardi et al., 1983; Busetto et al., 1984; Gusi et al., 1987). This method is very simple and does not require a specific experimental apparatus. The only requirement is prolonged washing to reduce the amount of residual alkali because of the low solubility of the alkali bicarbonates. Examples of preparations carried out at different supersaturation conditions or using other methods have been reported in previous papers (Cavani et al., 1991; Clause et al., 1991; de Roy et al., 1992; Trifirò and Vaccari, 1996).

PILAC's may be prepared by different methods: i) exchange of inorganic anions, ii) exchange of organic anions, iii) structure reconstruction, and iv) direct coprecipitation (Cavani et al., 1991; Trifirò and Vaccari, 1996). In some cases, these methods have been combined in order to obtain more crystalline and ordered phases. For example Dimotakis and Pinnavaia (1990) used structure reconstruction of meixnerite, carried out in the presence of glycerol as a swelling agent, to produce anionic clays containing long-chain organic anions (e.g., adipate or toluensulphonate), which afterwards were exchanged with the

polyanions. For more detailed information on the different preparation methods of the PILAC's, reference should be made to previous reviews (e.g., Cavani et al., 1991; Trifirò and Vaccari, 1996).

3.2. Catalytic applications

Synthetic anionic clays, as such or, mainly, after thermal decomposition, find many industrial applications and probably more will be found in the future in totally unexpected areas (Cavani et al., 1991; Vaccari, 1992, 1998; Trifirò and Vaccari, 1996) (Fig. 6). Furthermore, although the available literature on anionic clays is currently less than that for cationic clays, anionic clays are the most promising precursors of multicomponent catalysts for many catalytic reactions of industrial interest, complementary to those of cationic clays. Catalytic applications of the mixed oxides obtained by their controlled calcination include polymerization of alkene oxides, aldol condensation of aldehydes and ketones, methane or hydrocarbon steam reforming, methanation, methanol synthesis, higher-alcohols or hydrocarbon (Fischer–Tropsch) synthesis, etc. (Cavani et al., 1991; Vaccari, 1992, 1998; Trifirò and Vaccari, 1996). Over the past few years there has been an exponential increase in the references relative to these applications, most of them of industrial interest. Furthermore, new applications or upgrading are continuously being reported, concerning both compositions and reactions.

In regard to the new compositions, besides those containing noble metals (Blom and Derouane, 1991; Bhattacharyya et al., 1995; Basile et al., 1996a;

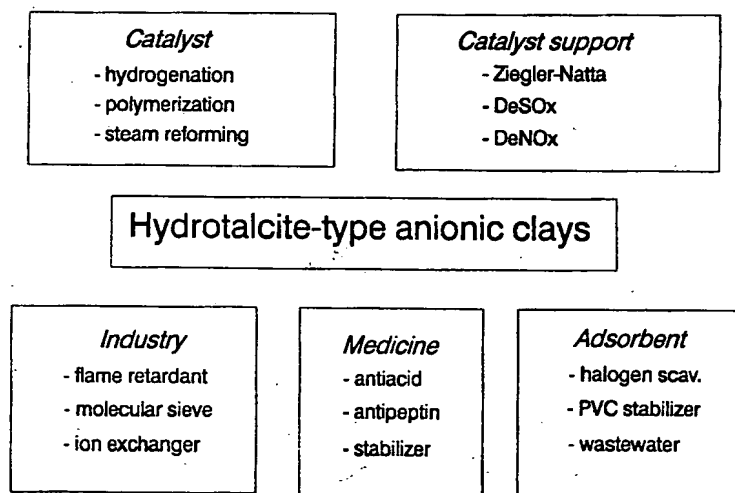


Fig. 6. Examples of industrial applications of HT anionic clays as such or after thermal decomposition (Cavani et al., 1991; Vaccari, 1992, 1998; Trifirò and Vaccari, 1996).

Basini et al., 1996), mention should be made of the recently reported synthesis of anionic clays exhibiting a sheet-like morphology, with sheet broadness to thickness ratios ranging from 100 to 2000 (Schutz et al., 1995; Kelkar and Schutz, 1997). New reactions worth mentioning here include the synthesis of aromatic compounds from alkanes (Blom and Derouane, 1991; Derouane et al., 1992, 1993) as well as that of intermediates or fine chemicals (Atkins and Chibwe, 1992; Forkner, 1993; Corma et al., 1994a,b; Rath et al., 1994; Velu and Swamy, 1994; Castiglioni et al., 1995, 1996a, 1998; Lin and Cheng, 1996; Figueras et al., 1998). In the field of environmental catalysis or upgrading regarding the use of energy resources, some new and promising applications can be cited such as the catalytic decomposition of N_2O (Table 9, Fig. 7) (Kannan and Swamy, 1994; Swamy et al., 1994; Armor et al., 1996; Centi et al., 1997), the selective catalytic reduction (SCR) of NO by NH_3 (Lojewski et al., 1997; Montanari et al., 1997; Trombetta et al., 1997) or the partial oxidation of methane to synthesis gas (Bhattacharyya et al., 1994, 1995; Basini et al., 1996, 1997; Basile et al., 1996a,b, 1998a,c).

γ -Butyrolactone (GBL) is an example of a small volume commodity of high economic relevance, considering that it is currently the most useful feedstock for the production on an industrial scale of *N*-methyl-pyrrolidone (NMP), which has suitable chemico-physical properties and is more environmentally acceptable than the present chlorine-based solvents (Castiglioni et al., 1996b, 1998). The replacement of chromite catalysts in the vapour phase hydrogenation of maleic anhydride (MA) to GBL was investigated due to the increasing restrictions on their use in light of the toxicity of the Cr^{6+} ions present in the spent catalysts.

Table 9

Catalytic activity of different mixed oxides obtained by calcination of HT precursors (Swamy et al., 1994)

Sample	Ratio	Calc. temp (K)	N_2O conversion (%)		
Co/Al	2.2:1.0	773	99 ^a	96 ^b	54 ^c
Co/Al	2.2:1.0	1073	12 ^a	n.d.	n.d.
Cu/Al	2.0:1.0	823	48 ^a	n.d.	n.d.
Co/Al	3.0:1.0	773	84 ^a	67 ^b	25 ^c
Ni/Al	3.0:1.0:1.0	773	95 ^a	92 ^b	99 ^c
Co/Mg/Al	2.0:0.94:1.0	773	100 ^a	97 ^b	79 ^c
Rh/Co//Al	0.3 wt.% Rh	773	100 ^a	99 ^b	88 ^c
Rh/Co/Al	0.7 wt.% Rh	773	100 ^a	100 ^b	100 ^c
Rh/Co/Al	1.0 wt.% Rh	773	71 ^a	42 ^b	12 ^c

Experimental conditions: atmospheric pressure; reaction temperature = 723 K; GHSV = 30,000 h^{-1} .

^a N_2O 985 ppm and the remainder He.

^b N_2O 985 ppm, O_2 = 25,000 ppm and the remainder He.

^c N_2O 985 ppm, O_2 = 25,000 ppm, H_2O = 20,000 ppm and the remainder He.

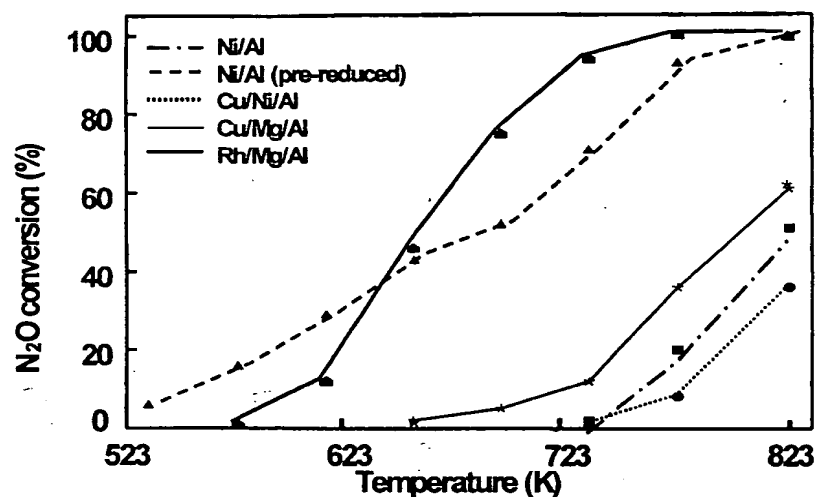


Fig. 7. Comparison of the activity in the conversion of N_2O for various mixed oxides obtained from HT precursors by calcination at 923 K for 14 h. Experimental conditions: atmospheric pressure; N_2O = 10,000 ppm and the remainder He, GHSV = 1800 h^{-1} (Centi et al., 1997).

Cu/Zn/Al catalysts with the right composition gave rise to complete MA conversion and high yields in GBL, with, furthermore, very low by-products and tar formation (Table 10) (Castiglioni et al., 1996a). Vapour phase hydrogenation of MA to GBL using Cu/Zn/Al catalysts may actually be considered a significant example of a clean and economically viable process, considering that it is the most direct way to produce GBL, without using hazardous feedstocks and avoiding problems related to disposal of the catalysts, and it can be

Table 10

Catalytic activity of the catalysts with atomic ratio Cu/Zn = 0.5 and different aluminum content (as atomic ratio percent) in the hydrogenation of a solution of maleic anhydride in γ -butyrolactone (60:40 wt.%) (Castiglioni et al., 1996a)

	Al = 24.0%		Al = 17.0%	
	518 K	548 K	518 K	548 K
MA conversion (%)	100	100	100	100
GBL yield (%)	81	96	79	88
SA yield (%)	6	0	0	0
THF yield (%)	< 1	2	1	2
Other yield (%)	5	2	2	9

Experimental conditions: pressure = 0.1 MPa; H_2/C_4 ratio in the feed = 170 mol/mol.

MA = maleic anhydride; GBL = γ -butyrolactone; SA = succinic anhydride; THF = tetrahydrofuran; Others = by-products, mainly *n*-butanol and butyric acid.

integrated with the production of MA from *n*-butane (Castiglioni et al., 1995, 1996a,b, 1998).

Reactions such as the SCR of NO and methane activation are also subjects of high scientific and industrial interest. In the former reaction, anionic clays containing transition elements have been investigated, and general improvements in the catalytic performances were found in comparison to the analogous supported catalysts (Gazzano et al., 1996). Considering that a Cu-containing catalyst exhibited the best catalytic behaviour, Cu-containing anionic clays were thoroughly investigated as a possible inexpensive alternative to Cu-zeolites, mainly Cu-ZSM-5. In these studies it was found that the presence of stabilized copper ions improved the catalytic performances in the presence of excess O₂ (such as present in flue gases) (Fig. 8), with very interesting catalytic performances obtained for Cu-contents in the range 12 to 25 wt.% ca. (as CuO), associated to good stability with time-on-stream (Fig. 9) (Lojewski et al., 1997; Montanari et al., 1997). The reaction mechanism and the nature of the active sites involved either in SCR of NO or ammonia oxidation (the most important side-reaction observed at high temperature), have been investigated by FT-IR spectroscopy by means of different probe molecules, showing that the SCR reaction occurs between gas-phase NO and NH₃ strongly adsorbed on Cu-containing phases and/or highly dispersed CuO clusters (Trombetta et al., 1997). Moreover, the SCR activity of these catalysts did not involve Brönsted acid

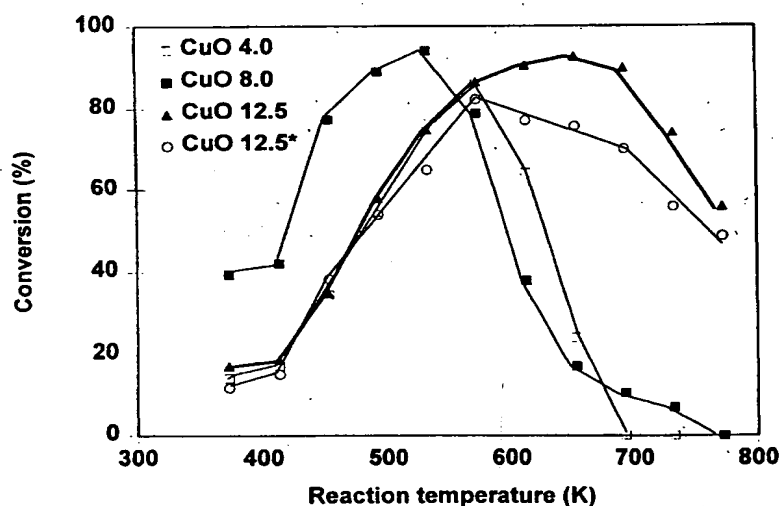


Fig. 8. Catalytic behaviour in NO reduction with NH₃ and O₂ of Cu/Mg/Al mixed oxide catalysts with different Cu-content (as CuO wt.%), obtained from HT anionic clays by calcination for 14 h at 923 K or 1173 K (*). Experimental conditions: atmospheric pressure; NO = 6000 ppm, NH₃ = 7500, O₂ = 30,000 ppm and the remainder He; GHSV = 10,000 h⁻¹ (Lojewski et al., 1997; Montanari et al., 1997).

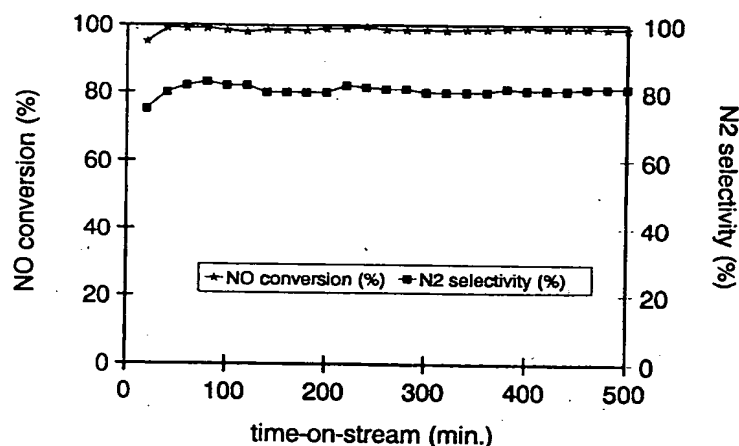


Fig. 9. Catalytic activity as a function of time-on-stream at 653 K in NO reduction with NH_3 and O_2 of a Cu/Mg/Al mixed oxide (CuO = 12.5 wt.%) obtained from a HT precursor by calcination for 14 h at 923 K. Experimental conditions as in Fig. 7 (Montanari et al., 1997).

sites, absent on the surface of these samples, thus evidencing that Brönsted acidity is not always a key requirement for SCR activity.

The catalytic partial oxidation (CPO) of methane represents a promising way to reduce the price of synthesis gas in comparison to the current production technologies (e.g., Rostrup-Nielsen, 1984, 1994; Rodler and Twigg, 1989; Solbalken, 1991; Sundset et al., 1994). This reaction has been extensively studied in recent years; however an industrial process based on catalytic substoichiometric combustion has not yet been developed and commercialized. CPO reactions can occur at very short residence times, leading to the introduction of small reactors and advantageous process conditions (Basini et al., 1995). Therefore, we investigated the reactivity at very short residence times [namely, the molecular aspects of the reaction mechanism and the role of catalytic and homogeneous gas phase reactions (Basini et al., 1997)] as well as the role of catalyst composition, activation procedure and reaction parameters (Basile et al., 1996b, 1998a). In order to compare samples obtained from precursors having the same structure and taking into account the superior stability of catalysts obtained from anionic clays, these phases have been widely employed. New HT phases containing noble metal ions also have been synthesized. Calcination and reduction of these phases gave rise to catalysts with very interesting values of methane conversion and selectivity in synthesis gas (Fig. 10) (Basini et al., 1996; Basile et al., 1996a, 1998b). These catalysts also showed interesting performances in the catalytic total oxidation (Basile et al., 1998b) and CO_2 -reforming (Basile et al., 1998d) of methane, with specific behaviours associated to the nature of the different active elements present. Considering that HT phases can be useful precursors of multicomponent catalysts, the study of the activity in

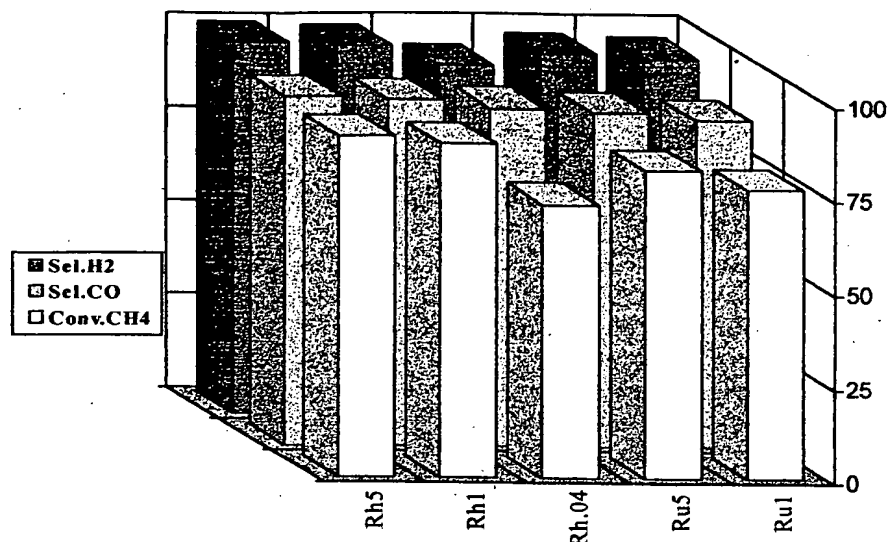


Fig. 10. Activity in the CPO of methane as a function of the Ru- or Rh-content for catalysts obtained from HT precursors by calcination at 1173 K for 14 h. Experimental conditions: oven temperature = 1023 K, contact time = 7.2 ms, reaction gas mixture = $\text{CH}_4/\text{O}_2/\text{He} = 2:1:4$ (v/v). The catalysts were previously reduced at 1023 K for 5 h in a 7 l/h flow of an equimolar H_2/N_2 mixture (Basile et al., 1998b).

the CO_2 -reforming and CPO reaction at short residence time has been extended to Rh/Ni-containing catalysts, evidencing possible synergic effects between the metals (Basile et al., 1998c).

Moreover, for widely studied subjects, space is again available and new and interesting results have also been recently reported, such as for example those on the phases responsible for the high thermal stability of Ni/Al and Ni/Mg/Al catalysts (Clause et al., 1991; Trifirò et al., 1994; Vaccari and Gazzano, 1995) or those referring to the stereospecific polymerization of propylene oxide on Mg/Al mixed oxides, with formation of a crystalline, isotactic polymer fraction (Laycock, 1990). Also very recently superior activity and stability in CO_2 /steam reforming of methane, especially under severe reaction conditions, of Ni/Al catalysts derived from HT phases have been claimed in comparison to commercial Ni/ Al_2O_3 catalysts and traced back to the specific structure of the precursors (Bhatthacharyya et al., 1998). Furthermore, on the basis of X-ray and neutron diffraction data it has been possible to shed light on the location of the elements in the different phases present in Ni/Al and Ni/Mg/Al catalysts (Vaccari and Gazzano, 1995; Gazzano et al., 1997).

Referring to the applications of basic Mg/Al catalysts, of particular importance is the possibility to substitute liquid bases, such as ammonia, ammonium salts or amines, developing environmentally friendly solid catalysts that can be

easily separated and recycled. Promising and charming applications have been recently reported in the field of fine chemicals and intermediates, regarding the one-step synthesis of citronitril (perfume as well as detergent and soap industry) (Corma et al., 1994b), chalcones and flavonoids (pharmaceutical industry) (Corma et al., 1994a), alkylated phenols (octane boosters and organic intermediates) (Velu and Swamy, 1994) and some high volume chemicals such as diacetone alcohol (Figueras et al., 1998; Tichit et al., 1998), α -isophorone (Kelkar and Schutz, 1998; Di Cosimo et al., 1998) and glycol ethers (Atkins and Chibwe, 1992; Forkner, 1993; Rath et al., 1994; Malherbe et al., 1998). Furthermore, in a very recent paper Ueno et al. (1998) reported a new application of Mg/Al hydrotalcites as efficient base catalysts for the epoxidation of various olefins using H_2O_2 in the presence of benzonitrile and with MeOH as the solvent (Fig. 11a). The same research team had reported in previous papers (Kaneda et al., 1995; Kaneda and Yamashita, 1996; Kaneda and Ueno, 1996) the interesting application of HT compounds containing small amounts of transition ions in the heterogeneous Baeyer–Villiger oxidation of various ketones using molecular oxygen and benzaldehyde, claiming a cooperative action between the basic sites and the transition metal sites in order to justify the increase in catalytic activity in comparison to the Mg/Al sample (Fig. 11b). Analogously, in the hydrogenation of CH_3CN on Ni/Mg/Al mixed oxides obtained from HT precursors (Cabello et al., 1997; Dung et al., 1998), very high values and conversion and selectivity in monoethylamine have been observed for a Mg/Mg + Ni ratio $\cong 0.23$, due to a compromise between the reducibility of the nickel (that affects the activity of the catalyst) and the acido-basicity of the catalysts (that is responsible for the formation of secondary products), both decreasing with the introduction of Mg^{2+} ions.

The textural and surface properties of the Mg/Al catalysts have been thoroughly investigated, and the possibility of modulating the activity as a function of the base strength needed for each reaction by an appropriate

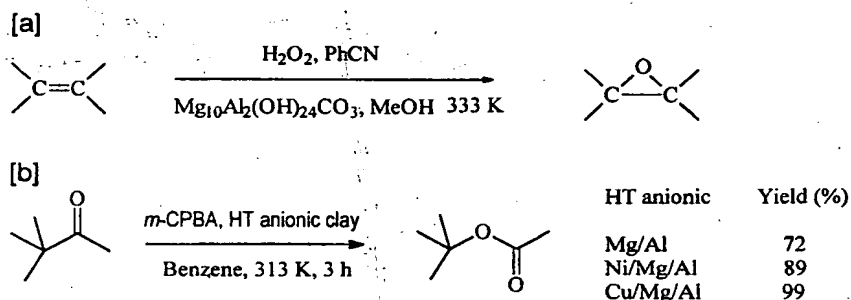


Fig. 11. Activity of different HT anionic clays in: (a) the epoxidation of olefins using H_2O_2 (Ueno et al., 1998), and (b) the Baeyer–Villiger oxidation of ketones (Kaneda et al., 1995; Kaneda and Ueno, 1996; Kaneda and Yamashita, 1996).

selection of the preparation conditions, Mg/Al ratio and calcination temperature has been shown (Rossi et al., 1991; Corma et al., 1994a; Rebours et al., 1994; Shen et al., 1994; Tsuji et al., 1994; Tichit et al., 1995; Guida et al., 1997). For example, with increasing Mg/Al ratio, the total amount of basic sites increases. This is mainly due, however, to the sites with $9.0 \leq pK \leq 13.3$, whereas the number of basic sites within $13.3 \leq pK \leq 16.5$ decreases (required, for example, in the condensation of benzaldehyde with ethyl bromoacetate) (Rossi et al., 1991; Corma et al., 1994a; Tichit et al., 1995).

Finally, anionic clays may also be useful precursors of supports of Ziegler–Natta catalysts for ethylene polymerization or DESO_x additives to FCC catalysts (Cavani et al., 1991; Yoo et al., 1992; Corma et al., 1994c), showing high stability also in severe reaction conditions, and excellent catalytic properties as well as catalyst regeneration. They also have been successfully used as supports of transition metal oxides for SCR of NO by NH₃, as alternatives to less stable supports such as active carbons (Gazzano et al., 1996). However, also in this field new applications continuously appear, such as for example that of vanadium oxides or noble metals supported on calcined Mg/Al HT anionic clays for the (i) oxidative dehydrogenation of *n*-butane (Blasco et al., 1995; López Nieto et al., 1995), (ii) synthesis of isobutyric aldehyde (Dinka et al., 1998), (iii) partial reduction of monocyclic aromatic hydrocarbons (Fukuhara et al., 1988), and (iv) synthesis of aromatic compounds (Blom and Derouane, 1991; Derouane et al., 1992, 1993).

Now, coming to PILAC's (as well as the intercalated clays), it must first of all be remembered that they have been prepared with the aim to create new useful networks for shape selective adsorption or catalysis. In the field of catalysis, their preparation has been claimed in order to fulfill the following objectives: i) to obtain shape-selective chemical, electrochemical or photo-catalysts, ii) to stabilize homogeneous or biomimetic catalysts in order to increase their service life and allow easy recovery and recycling, and iii) to prepare supported catalysts with concentrations of the active phase and activities higher than those obtained with conventional supports. Generally, PILAC's have been investigated at relatively low temperatures. Some applications however have been reported at temperatures at which serious doubts exist regarding their stability and in these cases the PILAC's must be more correctly considered as an alternative way to prepare homogeneous mixed oxides (e.g., Woltermann, 1984; Martin and Pinnavaia, 1986; Drezdon, 1988, 1990; Cavani et al., 1991; Tatsumi et al., 1992; Don Wang et al., 1995; Pinnavaia et al., 1995; Trifirò and Vaccari, 1996; Gardner and Pinnavaia, 1998; Hu et al., 1998; Vaccari, 1998).

Unlike for anionic clays, there is little information in the literature on the thermal evolution of PILAC's. Furthermore, the data which have been reported are not always in agreement and different interpretations and/or hypotheses have been made, probably as a result mainly of the different techniques employed or insufficient characterizations (Trifirò and Vaccari, 1996). Among

the different types of PILAC's, up until now only those containing iso and heteropolyanions have been investigated. For example, it has been reported that the interlayer space provides a reactive environment for oxovanadates, which upon gentle thermal treatment ($T > 433$ K) form at first, chain-like metavanadate species and then at higher temperature vanadates and oxides, while oxovanadates supported on alumina are stable up to 723 K (Tsu and Dutta, 1989, 1990). Analogously, the heteropolyanions in the PILAC's show decomposition temperatures significantly lower than those of the corresponding salts with large counterions, that may be attributed to a reaction of the mixed oxides obtained by dehydroxylation of the brucite-type sheets with the Keggin ions (Kwon and Pinnavaia, 1992; Wang et al., 1992). On the other hand, it seems evident that the thermal stability of anions such as phthalocyaninetetra-sulphonates, porphyrinetetra-sulphonates or metal complexes is not significantly modified by intercalation in the anionic clays and these compounds may be used only at low temperatures (≤ 333 K).

On the basis of the above considerations it is evident that PILAC's (as well as intercalated clays) may have mainly low temperature applications as such. Furthermore, at present they have been investigated only on a laboratory scale. PILAC's containing iso or heteropolyanions have been investigated in photolytic conversion of isopropanol to acetone under argon or oxygen, evidencing significant increases in activity despite the scattering of the host particles (Kwon et al., 1988; Kwon and Pinnavaia, 1992). Therefore, the realization of shape selective photochemical processes by controlling the pore size between the pillars, such as in zeolites may be hypothesized. The ability of HT compounds to incorporate anionic species while preserving their photochemical behaviour has also been reported for ruthenium complexes (Giannelis et al., 1987).

As examples of promising applications, at the end of this section, I should like to cite the interesting results obtained using phthalocyanins intercalated in Mg/Al anionic clays in the catalytic autoxidation reactions of 1-decanethiol and 2,6-di-*t*-butylphenol, chosen as probe molecules for the possible use in waste water purification treatment at room temperature (Pérez-Bernal et al., 1991; Chibwe and Pinnavaia, 1993). An increase in both activity and stability (Fig. 12), together with the possibility to recover the catalyst simply by filtration was found. The increase in stability observed was attributed to the inhibition of the dimerization process through intercalation in the HT structure. Mention also should be made of the recently reported elimination of contaminant thiols under ambient conditions, by oxidation with molecular oxygen using Mo^{VI} complexes intercalated in Mg/Al HT anionic clays (Cervilla et al., 1994a,b). The authors claimed that one of the advantages is the fact that water can be used as a solvent, although the results referred only to tests carried out using ethanol as the solvent. Furthermore, the preparation of HT-modified electrodes for specific applications in electroanalysis or electrocatalysis also may be considered very exciting and promising (Itaya et al., 1987; Keite et al., 1991; Mousty et al.,

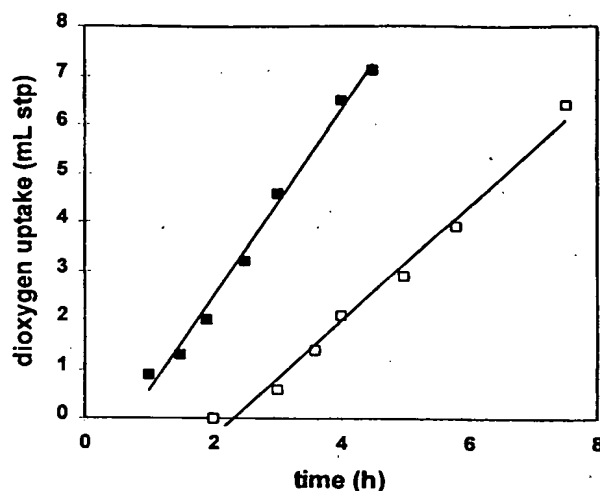


Fig. 12. Dioxygen uptake plots for the autoxidation of 1.5×10^{-2} M 1-decanethiol in the presence of Co(II)-phthalocyaninetetrasulphonates: (□) homogeneous catalyst (deactivated after one reaction cycle), (■) catalyst intercalated in a HT Mg/Al compound (no loss in activity after five consecutive reaction cycles). Experimental conditions: $T = 308$ K, $\text{pH} = 9.25$, substrate/cobalt ratio of 154 (Pérez-Bernal et al., 1991).

1994; Qiu and Villemure, 1995; Therias and Mousty, 1995; Ballarin et al., 1998a,b; Therias et al., 1998).

4. Conclusions

Environmental issues as well as process optimization requires the replacement of liquid acids or bases by more friendly solid catalysts. Cationic and anionic clays not only fulfil these requirements, but a broad spectrum of applications exists, and even more will be found in the future in unexpected areas, due to the possibilities of designing catalysts tailored for specific reactions and/or substrates. Furthermore, although montmorillonite, as such or modified, was the clay used in most of the applications reported in this paper, it is just one among the many smectites and there are many other, very different families of clay minerals. Of equal importance is the high flexibility and potential of synthetic anionic clays as precursors of multicomponent catalyst, due to the large number of composition and preparation variables that may be adopted. In addition, the complementarity between the applications of cationic and anionic clays, that cover a wide number of reactions of scientific and industrial interest must be noted. Moreover, all scientific knowledge acquired for cationic clays can also be applied to anionic clays with the necessary adaptations. In particular, we refer to the promising area of the synthesis and applications of PILAC's, for which,

however, interlayer accessibility and thermal stability have not been sufficiently investigated to discover whether or not these materials may have real applications as such, and not only as oxides obtained by their thermal decomposition.

In conclusion even though a large amount of work has been done, still more remains to be done. However, to exploit completely this potential cornucopia of catalytic applications a multidisciplinary approach is required, in which mineralogical, organic and industrial researchers collaborate, each contributing their specific knowledge. Exciting future prospects include the use of films, coated glass or metal wall supports (instead of divided particles in suspension) in liquid phase reactions and, even more of industrial interest, the synthesis of large amounts of products in the vapour phase, with continuous production and economic advantages.

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Clays

Controlling
the

Environment

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EDITORS

G.J. Churchman
CSIRO Division of Soils,
Private Bag No.2,
Glen Osmond, South Australia,
Australia, 5064

R.W. Fitzpatrick
CSIRO Division of Soils,
Private Bag No.2,
Glen Osmond, South Australia,
Australia, 5064

R.A. Eggleton
Department of Geology,
The Australian National University
Canberra, ACT,
Australia, 2600

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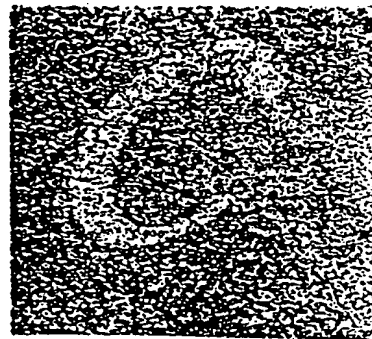
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CLAY CATALYSTS: OPPORTUNITIES FOR USE IN IMPROVING ENVIRONMENTAL QUALITY

Thomas J. Pinnavaia

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824, USA

Abstract

The use of clay minerals for improving environmental quality can take two approaches. One strategy is to tailor the clay either as an adsorbent or as a catalyst for remediation processes to correct already polluted environments. The second, and more desirable, strategy is to utilise the clay for 'green' chemical processing, wherein reagents are converted to products in essentially quantitative yields with little or no polluting byproducts. The present paper focuses on the properties of cationic (smectitic) and anionic (hydrotalcite-like) clays as catalysts for potentially benign chemical processes.

Keywords: catalysts, alkylation, nucleophilic displacement, smectites, hydrotalcites, acid rain, adsorbents, biomimetic

SMECTITE CLAY CATALYSTS

There are several properties of smectitic clays that make them interesting from a catalytic standpoint. One is that these are versatile cationic exchangers, so that a variety of ions can be introduced into the gallery region of the clay. Also, they can swell so that various molecules can be accommodated in the gallery and accessed for possible chemical reaction. An equally important property is the relative chemical inertness of the siloxane gallery surfaces. The layers of a smectite clay can be exfoliated and then reassembled without change in the oxygen framework. This chemical robustness is a great benefit in any chemical design approach. Some significant disadvantages of smectite clays are their colloidal particle size and the high degree of layer stacking disorder. These latter properties sometimes frustrate efforts to obtain accurate structural information. But in the absence of

such structural defects, we probably would not be able to realise the full advantages of the first three properties.

Alkylation catalysis

Among all of the smectite clay derivatives that have properties relevant to chemical catalysis, metal oxide pillared derivatives are especially important (Vaughan, 1988). These are microporous smectite intercalates formed by replacing the simple alkali metal or alkaline earth ions in the pristine mineral with a polycation that acts as a pillar precursor. Upon calcination the intercalated polycation is converted to a nanoscopic metal oxide particle with a structure that resembles a bulk oxide. Many pillar compositions have been prepared, including metal oxides of aluminium, gallium, titanium, among others (Burch, 1987). By far the most important metal oxide pillared clays are those that incorporate aluminium oxide as the pillaring species. The

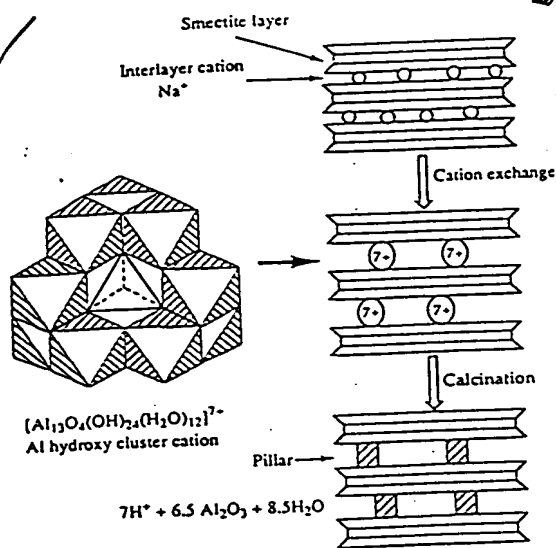


Fig. 1 Schematic illustration of the preparation of metal oxide-pillared clays and the structure of the alumina pillaring agent $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$.

pillaring agent used for the preparation of alumina pillared clays is the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ cation (Johansson, 1960). Figure 1 illustrates the general procedure for the preparation of an alumina pillared clay, along with the structure of the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ ion. One feature of the Al_{13} polycation precursor is that it has a van der Waals thickness comparable to the thickness of the smectite lattice itself. Four atomic planes of oxygen atoms constitute the polycation. Twelve of the 13 aluminium atoms are in 6-fold coordination in the centres of octahedra, and the 13th aluminium is located in the centre of a tetrahedral coordination sphere of oxygen atoms in the centre of the polyhedron. When this ion is heated in the gallery of the smectite clay it undergoes dehydration and dehydroxylation to form a small aggregate of aluminium oxide with approximate dimensions of 10 Å in diameter. Thermal dehydration of the ion results in the formation of coordinatively unsaturated sites at the aluminium centres, which can function as Lewis acid sites. Also, in order to balance the negative charge of the layered silicate framework, protons are released to basic sites in the layers. Consequently, metal oxide pillared clays are both Bronsted and Lewis acids. It is this feature of their chemistry that makes them interesting as catalysts.

An important class of organic reactions known as electrophilic substitutions have been of industrial importance for many decades. These reactions, which are as old as chemistry itself, include Friedel-Crafts processes in which alkyl groups are added to an aromatic nucleus. Anhydrous metal halides and other Lewis acids are normally used to activate alkylating agents such as alkyl chlorides. Another type of conventional catalyst for this kind of chemistry are Bronsted acids such as sulfuric acid. The acid protonates alkylating agents such as alcohols and olefins, and the resulting carbocations attack the arene ring to give

the alkyl-substituted product. Chemical industries based on dyes, polymers, plastics, and so forth, would not exist without alkylation chemistry. However, one pays an environmental price for the use of these catalysts. For instance, anhydrous aluminium trichloride is really a very poor catalyst for aromatic alkylations. An almost stoichiometric amount of aluminium trichloride is needed for every mole of alkylating agent. Therefore, there is a disposal problem in utilising these materials on an industrial scale. When sulfuric acid is used as a catalyst for alcohol alkylating agents, water is produced. The sulfuric acid eventually loses its catalytic activity through dilution and must be replaced. Thus, another disposal problem is created, making aromatic alkylations expensive and environmentally undesirable. What is needed is a recyclable solid acid catalyst as a replacement of these homogeneous Lewis and Bronsted acids.

Alumina pillared clays show considerable promise as recyclable acid catalysts (Figueras, 1988). The Lewis and Bronsted acidity of metal oxide pillared clays can be manifested in part by the chemisorption of pyridine. Shown in Figs 2A and B are the ring stretching frequencies of pyridine adsorbed on two aluminium oxide pillared clays: one an alumina pillared fluorohectorite with a surface area near 200 m² per gram and the other an alumina pillared montmorillonite with a surface area near 300 m² per gram (Burruille and Pinnavaia, 1993). These surface area values are typical of aluminium oxide pillared smectite clays. The ring stretching frequency characteristic of protonated pyridine, the so-called Bronsted pyridine bound to coordinatively unsaturated Lewis acid sites on the aluminium oxide pillars appears near 1450 cm⁻¹.

Zeolites are another well-known family of porous metal oxides. These materials are open framework aluminosilicates with compositions similar to pillared clays. The chemisorption of pyridine on acidic zeolite derivatives, such as the commercially important acid zeolite H⁺ mordenite, occurs primarily on Bronsted acid sites. In comparison to an aluminium pillared clay, mordenite has a much greater Bronsted acidity and very little Lewis acidity. Another striking feature of H⁺ mordenite is the surface area of 650 m² g⁻¹, which also is substantially higher than the pillared clay. In a catalytic reaction where Bronsted acidity is important, one might expect, on the basis of the higher surface area and greater Bronsted acidity that the zeolite

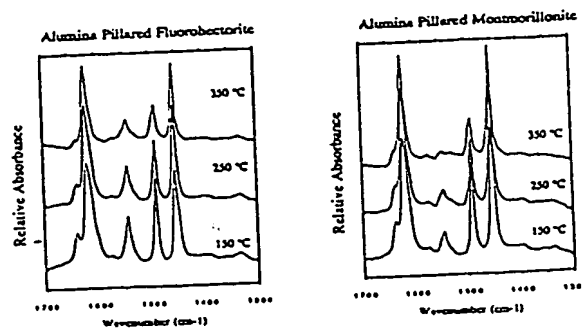


Fig. 2 FTIR spectra of the ring stretching frequencies of pyridine chemisorbed on alumina pillared derivatives of fluorohectorite and montmorillonite.

catalyst would be much more active as a Friedel-Crafts catalyst than an alumina pillared clay. But, this is not the case.

Consider the alkylation of liquid phase biphenyl 250°C with propene as the alkylating agent (Butruille and Pinnavaia, 1992). In this reaction protons attack the double bond of the propene, giving the protonated propyl cation, which then attacks the aromatic ring and eventually leads to electrophilic displacement of a proton by the alkyl group. Mordenite affords 57% conversion of biphenyl at a ratio of 30 g of biphenyl to 0.2 g of catalyst. If the same amount of alumina pillared montmorillonite is used in place of mordenite, the conversion of the substrate to the final alkylated products is higher, about 67%. Alumina fluorohectorite is an even more potent alkylation catalyst. About one-third the amount of catalyst used in the mordenite reaction is needed to obtain comparable conversions. Thus, the replacement of hydroxyl groups in the 2:1 silicate layers by fluorine enhances the Bronsted acidity of the pillared structure. We suggest that the pillared clays are generally more effective as acid catalysts than zeolites. Despite their lower acidities and surface areas, pillared clays are less hydrophilic than zeolites. In contrast, zeolites are very sensitive to the presence of trace amounts of water. Water competes very effectively with organic molecules for adsorption sites and blocks the internal channels of the zeolite. This limits access to the zeolite acid sites and decreases the effectiveness of zeolites for Bronsted catalysis. On the other hand, the pillared clays have a lower affinity for contaminating polar molecules like water and are better able to accommodate organic substrates. Therefore, pillared clays can be much more effective solid acid catalysts than zeolites. Results such as these suggest that the future is very bright for the utilisation of metal oxide pillared clays in 'green' chemical processing.

Phase transfer catalysts

Another very important type of reaction in organic chemistry is the nucleophilic displacement reaction. It has been recognised for some time that quaternary alkylammonium ions are effective catalysts for the displacement of leaving groups from electrophilic carbon centres (Dehmlow and Dehmlow, 1983). In typical nucleophilic displacement processes, the in-coming group is an inorganic species such as cyanide, halide or hydroxide ion. These nucleophiles are soluble primarily in aqueous media. The substrate, the organic reagent in the reaction, is usually soluble only in an organic solvent. Consequently, the immiscibility of the aqueous and the organic phases precludes efficient reaction. Quaternary onium ions are capable of trans-

ferring the inorganic reagent into the organic phase by forming an ion pair with the inorganic nucleophile (Dehmlow and Dehmlow, 1983). The transferred ion pair reacts with the organic substrate to give the final products. There has been interest by the industrial community to utilise this desirable catalytic chemistry. However, there are complications, one of which is environmentally related. Onium ions are surfactants, and they have to be removed entirely from the aqueous phase before disposal as a waste stream. Also, onium ions are relatively expensive and must be recovered regardless of environmental considerations. These factors have contributed to the limited use of alkylammonium ions as catalysts for nucleophilic displacement reactions.

One way of dealing with the onium ion recovery problem, as originally suggested by Regen (1976), is to immobilise the ion on the surface of a solid. This strategy is illustrated in Fig. 3. The organic reagent would be removed from the organic solution at the interface with a solid. At the same time, the inorganic reagent would move from the aqueous liquid phase to the interface of the solid. The two reagents, meeting at the solid interface, react to form products, which diffuse back into the liquid phases in which they were soluble. This type of process was termed 'triphasic catalysis' by Regen (1976). Polymers were initially used as immobilising agents, but the supported onium ions were relatively unreactive owing to difficulties in swelling the polymer and accessing the onium ions. Functionalised metal oxides also have been used to immobilise onium ions (Tundo *et al.*, 1982). The problem with these oxides, however, was the hydrolysis and subsequent desorption of the onium ions from the solid surface. Thus, the lifetimes of the catalysts were not acceptable for practical applications.

We have found that certain organic clays are very attractive materials for triphase catalysis (Lin and Pinnavaia, 1991; Lin *et al.*, 1992). Based on the recent work of Lagaly (1986), it is known that alkylammonium ions, when intercalated in clays, adopt orientations that depend very much on the charge density of the host layer. For instance, at very low charge densities, long chain alkylammonium ions intercalate with the long chain axes parallel to the host layers. As the layer charge increases, lateral bilayers, pseudo trimolecular layers and even paraffin type structures can form. The assembly of the onium ions determine the wetting properties of the clay surfaces by different liquids. For instance, organoclays with low charge density are wet by water. However, higher charge density organoclays with lateral bilayer orientations of the onium ion chains are amphiphilic, that is,

Table 1 Triphase nucleophilic displacement reactions carried out in the presence of $[(n-C_8H_{17})_4NMe]^+$ -hectorite

Substrate	Nucleophilic Reagent	Substrate to Onium Ion mole ratio	Time/Temp	Product	Yield (%)
$n-C_8H_{17}Br$	C_6H_5OH (3 mol)/2.5 M NaOH	100	1.5 h/90°	$n-C_8H_{17}OC_6H_5$	83
$n-C_8H_{17}Br$	NaSCN (10 mol)	200	1.5 h/90°	$n-C_8H_{17}SCN$	99
$n-C_8H_{17}Br$	NaS (6 mol)	100	0.5 h/90°	$(n-C_8H_{17})_2S$	91
$n-C_8H_{17}Br$	$C_6H_5CH_2CN$ (19 mol) 50% NaOH	100	65 h/50°	$(n-C_8H_{17})CH(CN)C_6H_5$	86
$C_6H_5CH_2OH$	10% NaOCl (7 mol)	40	10 h/50°	C_6H_5CHO	83

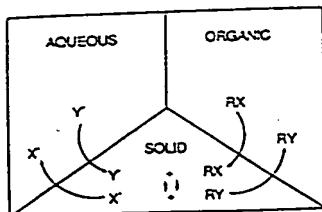
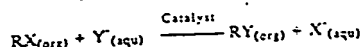


Fig. 3 The process of triphase catalysis: an inorganic nucleophilic reagent (Y) in aqueous solution and an organic substrate (RX) in organic solution are transferred to the surface of a solid (organoclay) where they undergo reaction to form new products (X' and RY), which diffuse back into the liquid phases in which they are soluble. The catalyst is easily separated from the reaction mixture by filtration or centrifugation.

capable of being wetted both by water and by organic liquids. Bilayer structures are very efficient for triphase catalysis.

The methyltriocetylammmonium exchanged form of hectorite exhibits a basal spacing corresponding to a lateral bilayer structure. Table 1 compares the pseudo first order rate constants for several nucleophilic displacement reactions in the presence of this organoclay. Note that the organoclay affords very high yields over a wide range of nucleophiles. Performance properties such as these suggest that organoclays should receive serious consideration for use as environmentally benign catalysts.

LAYERED DOUBLE HYDROXIDES OR ANIONIC CLAYS

We consider next the second family of clays for possible environmental applications, the so-called layered double hydroxides (LDHs), hydrotalcite-type clays, or anionic clays (Cavani *et al.*, 1991; de Roy *et al.*, 1993). As is illustrated in Fig. 4, LDHs are complementary to smectite clays insofar as the layers are positively charged with exchangeable gallery anions intercalated between the layers. LDHs have magnesium hydroxide or brucite-like structures, but instead of all the M^{2+} divalent ions occupying the octahedral interstices of the hydroxide layers, trivalent M^{3+} ions occasionally substitute for the divalent ions. This substitution imparts a net positive charge on the hydroxide layers which is balanced by the gallery anions. The overall composition can be expressed as $[M_1^{2+}, M_2^{3+}(\text{OH})_2][A^{n-}]_n \cdot zH_2O$, where A^{n-} represents the gallery exchange anion. One can introduce a variety of gallery anions as well as layer cations into LDH structures. Typically the anionic exchange capacities of LDHs are four times as large as the cation exchange capacity of a smectite clay. They have relatively high external surface areas ranging approximately from 30 to 150 $\text{m}^2 \text{g}^{-1}$. Especially attractive from a catalytic standpoint are the diverse chemical compositions that one can achieve depending on the nature of the gallery anions and metal ions in the brucite-like layers. The other advantage to these materials is that they can often be synthesised by one-step coprecipitation methods.

Sorption of acid rain precursors

One possible use of the basic properties of layered double hydroxides is as sorbents for acid anhydrides. These are small,

Layered Double Hydroxide

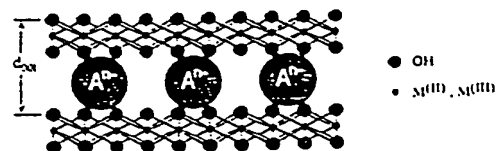


Fig. 4 Schematic illustration of the structure of an anionic layered double hydroxide clay. A^{n-} are the gallery exchange anions.

non-metal oxide molecules such as sulfur dioxide and nitrogen oxides. These latter oxides are important players in acid rain formation, which, in large part, results from the burning of sulfur-containing coal in power plants. The sulfur impurities are converted to SO_2 , and some SO_3 in the combustion process. These gaseous anhydrides are released into the atmosphere along with the rest of the flue gases. Eventually, the SO_2 is oxidised to SO_3 in the atmosphere, where it becomes hydrated by reaction with water to form sulfuric acid and, ultimately, acid rain. The nitrogen in the combustion air of a coal-fired boiler and nitrogen impurities in the coal also contribute to the formation of nitrogen oxides, which develop into a nitric acid component of acid rain.

One approach to removing acidic SO_2 and SO_3 emissions from flue gas is to inject a base such as lime or limestone into the boiler. The sulfur oxides adsorb on the base formed and become trapped as particles of calcium sulfite and sulfate which then can be removed along with other particulates in the bag house or in the electrostatic precipitator. Such acid-base reactions do occur under the conditions encountered in a boiler, but the problem is one of reactivity. This is illustrated in Fig. 5, curves A, B, and C for the reaction of lime (CaO), hydrated lime ($\text{Ca}(\text{OH})_2$), and limestone (CaCO_3) with SO_2 . At the initial stages of the reaction there is very rapid reaction uptake of the SO_2 , but the reaction rates soon decrease dramatically due to the formation of passivating skin of calcium sulfate or calcium sulfite at the surface of the lime particles. In other words, the internal regions of the particles are no longer accessible for reaction with SO_2 or SO_3 . What is needed is a more reactive basic adsorbent.

We have been investigating the properties of basic layered double hydroxides as high temperature adsorbents for SO_2 (Amarasekera and Pinnavaia, unpublished data). Some of the more reactive LDHs have compositions of the type $\text{Ca}_{1-x}\text{Al}_x(\text{OH})_2[\text{CO}_3]_{x/2}$. However, the reactivity of these LDH materials toward SO_2 is not significantly different from that of ordinary lime. The initial reactivity over very short times is very high, but, as in the case of lime, once a skin of calcium sulfite or sulfate is formed on the particle, the reaction rate decreases dramatically, and only a small fraction of the total LDH is consumed in the reaction. Since sulfur trioxide is much more reactive than sulfur dioxide towards a variety of bases, we thought it might be possible to catalyze the oxidation of SO_2 to SO_3 by replacing some of the aluminium ions in the LDH structure with an oxygen transfer agent such as Fe^{3+} . The SO_2 molecule could be oxidised to SO_3 at the iron centre and immediately trapped at the calcium centre as calcium sulfate within the same particle. Fig. 5, curve D, illustrates the improvement in SO_2 reactivity as a result of introducing iron into the LDH structure. Comparing the relative reactivity of the mixed iron

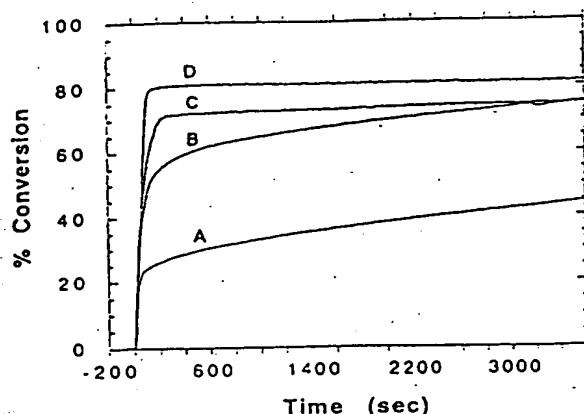


Fig. 5 SO_2 uptake curves for the reaction of SO_2 with layered double hydroxides: (A) CaO ; (B) $\text{Ca}(\text{OH})_2$; (C) CaCO_3 ; (D) $[\text{Ca}_2\text{Al}_{0.4}\text{Fe}_{1.6}(\text{OH})_{10}\text{CO}_3] \cdot x\text{H}_2\text{O}$.

aluminium calcium LDH to the conventional lime absorbents derived from calcium carbonate, we see that the LDH is an excellent performer, especially at very low reaction times. This is another area that may provide opportunities for environmental quality improvements based on remediation.

Biomimetic catalysis

Let us consider one other potential application of layered double hydroxides. Certain types of biomimetic catalysts, such as porphyrin and phthalocyanine metallomacrocycles, can be intercalated into layered double hydroxide galleries (Pérez-Bernal *et al.*, 1991; Chibwe and Pinnavaia, 1993). One of the attractive features of these macrocycles is that they are capable of activating dioxygen or peroxides for the oxidation of organic molecules at ambient or near ambient temperatures. Also, the metallomacrocycle can be made anionic and, hence, suitable for intercalation in LDH structures by replacing hydrogen atoms on the macrocycle by carboxylate or sulfate. Macrocycles such as cobalt(II) phthalocyanines are capable of catalyzing the oxidation of foul-smelling thiols to less obnoxious disulfides. Another type of molecule that is environmentally unfriendly is the phenols. Cobalt(II) phthalocyanines are also capable of oxidising phenols to polyphenylene quinones, which are insoluble in water and easily separated from the environment by filtration.

When cobalt(II) phthalocyanine tetrasulfonate is intercalated into an LDH gallery, it adopts an edge-on orientation relative to the gallery surfaces. This orientation allows the metal centres near the edges of the galleries to be accessible for reaction with molecules from solution. Substantial reaction rates are observed even though metal centres at the internal regions of the galleries may not be accessible to the substrate. Fig. 6 illustrates the uptake of oxygen for the oxidation of decane thiol to the corresponding disulfide in the presence of cobalt(II) phthalocyanine tetrasulfonate intercalated in a $\text{Mg}_{0.6}\text{Al}_{0.4}\text{LDH}$. Note that the intercalated catalyst is even more reactive than the homogeneous catalyst, the respective oxygen uptake rates being 109 and 52 nmole of dioxygen per mole of cobalt per minute. But more importantly, the clay catalyst is indefinitely stable and can be filtered and reused over and over again. In contrast, the homogeneous catalyst is totally deactivated and

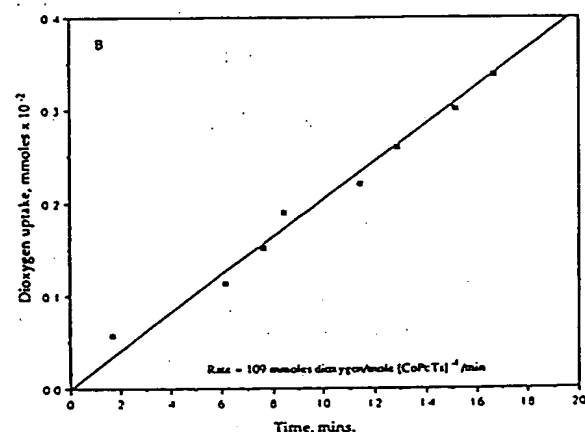
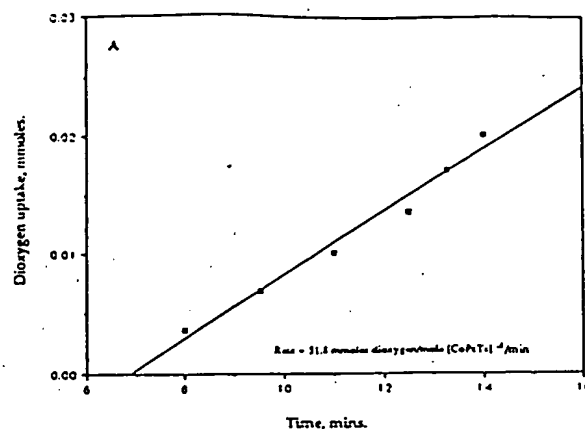


Fig. 6 Dioxygen uptake curves for the oxidation of 1-decanethiol in the presence of cobalt(II) phthalocyanine tetrasulfonate: (a) homogeneous catalyst (b) heterogeneous catalyst intercalated into a $\text{Mg}_{0.6}\text{Al}_{0.4}\text{LDH}$

rendered useless in less than 25 turnovers. Catalyst deactivation in solution may result from dimerisation of the complex or from self oxidation. Immobilisation of the metallomacrocycle in the gallery of the LDH prevents the complexes from coming in contact with one another and thereby avoids destructive self oxidation reactions. Thus, the anionic hydrotalcite-type clays may also find future applications that lead to the improvement of environmental quality.

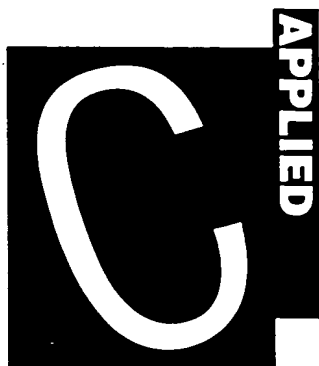
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Alumina pillared montmorillonite: characterization and catalysis of
toluene benzylation and aniline ethylation

Sankarasubbier Narayanan *, Kiranmayi Deshpande
Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India



Editors

Prof. H.H. Kung
Department of Chemical Engineering
Northwestern University
Room E136, 2145 Sheridan Road
Evanston, IL 60208-3120
USA
Fax: (+1-847) 4671018
E-mail: hkung@nwu.edu

Prof. K. Segawa
Sophia University
Dept. of Chemistry
7-1 Kioi-cho, Chiyoda-ku
Tokyo 102-8554
Japan
Fax: (+81-3) 32384350
E-mail: k-segawa@sophia.ac.jp

Prof. J.C. Vedrine
Leverhulme Centre for Innovative Catalysis
Department of Chemistry
The University of Liverpool
PO Box 147
Liverpool L69 7ZD
UK
Fax: (+44-151) 7943589
E-mail: vedrine@liverpool.ac.uk

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Alumina pillared montmorillonite: characterization and catalysis of toluene benzylation and aniline ethylation

Sankarasubbier Narayanan*, Kiranmayi Deshpande

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Abstract

Na montmorillonite (Wyoming, Source Clays, SWy-2) is modified by Ce exchange and by alumina pillaring. The interlamellar distance $d(001)$ of the pillared samples is measured by XRD. Surface area, total pore volume, external surface area (A_{ext}) and micropore volume (V_{mi}) of the samples are calculated from N_2 adsorption–desorption isotherms. Acidity of the samples is measured from the step wise temperature-programmed desorption (STPD) of ammonia. Samples are evaluated for aniline ethylation and toluene benzylation reactions. Almost equal BET and external surface area (A_{ext}) in Ce exchanged montmorillonite (Ce-Mont) suggest mesoporosity in the sample. Alumina pillared montmorillonite (AIPC(2)) and alumina pillared Ce exchanged montmorillonite (AIPC(Ce,2)) have almost the same micropore width and volume, suggesting the presence of micropores of similar size and number. The higher external surface area (A_{ext}) of AIPC (Ce,2) indicates comparatively more mesoporosity in the sample than in AIPC(2). The pillared samples are found to be thermally stable up to 873 K. Pillaring increased strong acidity, indicated by desorption of ammonia in the temperature region 573–723 K. Ce-Mont and AIPC(Ce,2) gave 100% conversion of benzyl alcohol. Over the same set of catalysts, aniline conversion is observed to be 55% and 81%, respectively. Low aniline and benzyl alcohol conversions (55% and 51%) are observed over AIPC(2), probably due to restricted diffusion of the reactants and products through the micropores. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Montmorillonite; Alumina pillaring; Toluene benzylation; Aniline ethylation

1. Introduction

Pillaring separates the layers of clay and supports them with bulky cations which can be metal oxide sol particles [1,2], metal clusters [3,4], or poly hydroxy metal ions [5–10]. Most commonly used poly hydroxy metal ions are Al [5,6], Zr [7], Cr [8], Ga [9] and Ti [10]. The process of pillaring is aided by two characteristic features of smectites viz., swelling

and transverse layer rigidity. Swelling, which is a reversible process, occurs on hydration of interlamellar cations and facilitates the process of ion exchange of bulky cationic species into the layers. Transverse layer rigidity, another intrinsic property of the smectite clays, helps in maintaining the interlamellar space between the pillars and prevents the gallery pores from collapsing.

Pillared clays are extensively studied as adsorbents [11] and as catalysts [12–14]. The modification produces a clay material with interesting physicochemical properties; for example, homogeneous distribution of micropores with mean pore diameters 0.7–0.9 nm,

* Corresponding author. Tel.: +91-40-715-3374; fax: +91-40-717-3757/3387.

E-mail address: snarayanan@iict.ap.nic.in (S. Narayanan).

surface area between 150 and 350 m² g⁻¹, availability of both Lewis and Bronsted acid sites and ability to catalyze various reactions such as alkylation [12], disproportionation [13] and hydrogenation [14].

Pore size, surface area, type and strength of acid sites and thermal stability of pillared clays have been found to be dependent on the pillaring species used. For example, Ti pillared clays are reported to possess large pores [15], zirconia pillared montmorillonites are rich in Bronsted acidity, while alumina pillared montmorillonites have a comparatively large number of Lewis acid sites [16].

For a particular pillared clay, the pore size and its distribution and the thermal stability depend on the method of pillaring [17]. The method of drying also seems to affect the porosity of the intercalated sample. Pinnavaia et al. [18] have reported that freeze-dried alumina pillared montmorillonite possesses large pores due to the house of cards arrangement of the layers; while the air-dried samples have a regular microporous structure. A homogenous distribution of pillars is obtained when the process of ion exchange is slow [17]. This happens when there is a competition between an already existing highly charged interlamellar cation and the pillaring cation. Based on these reports, in this investigation, montmorillonite was ion-exchanged with Ce prior to alumina pillaring with the idea to obtain a pillared clay which is homogeneously microporous and thermally more stable than the non exchanged pillared analogue. Hernando et al. [19] have studied the effect of Ce modification, but their investigations involve the effect of addition of the lanthanide to Al and GaAl pillaring solution on the catalytic properties of the pillared clays for isomerization and cracking reaction of *n*-heptane.

2. Experimental

2.1. Preparation of alumina pillared montmorillonite (AIPC)

The pillaring solution was prepared by hydrolysis of aqueous AlCl₃ with NaOH at different OH/Al ratios (1, 1.5, 2 and 2.25). NaOH (1 dm³, 0.1, 0.15, 0.2 and 0.225 M) was added drop-wise to AlCl₃ (1 dm³, 0.1 M) with constant stirring. During hydrolysis, the

temperature was maintained at 353 K. Later, the pillaring solution was aged for 15 h. A homogeneous slurry of Na-montmorillonite (Source Clays, SWy-2) was made by stirring a suspension containing 10 g of clay in 1 dm³ of distilled water. To this dispersion, the pillaring solution was added and the mixture was stirred for 6 h at 353 K. The ion-exchanged dispersion was filtered and washed free of Cl⁻ (filtrate was tested with AgNO₃). The intercalated clay was first air-dried and then calcined at 673 K for 5 h. The samples are identified as AIPC (*x*) where *x* represents OH/Al ratio: 1, 1.5, 2 and 2.25.

2.2. Preparation of alumina pillared Ce exchanged montmorillonite

A 5% suspension of Na-montmorillonite (Source Clays, SWy-2) was ion-exchanged with a solution of 0.1 M (NH₄)₂[Ce(NO₃)₆] for 38 h. The solution was changed at 8 h intervals. The ion-exchanged clay was washed, air dried and then calcined at 673 K for 5 h. A part of the Ce-exchanged montmorillonite was pillared with poly hydroxy Al(OH/Al = 2). The pillaring procedure described above is followed. The prepared sample is identified as AIPC (Ce, 2) after calcination at 673 K for 5 h.

2.3. Characterization

XRD of the representative samples (A-Na montmorillonite, B-Ce-Mont, C-AIPC(2) and D-AIPC(Ce,2)) was taken on a CGR theta 60 instrument with Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$). N₂ adsorption and desorption isotherms on the samples were constructed using Micromeritics ASAP 2010. From the data, BET and Langmuir surface area, external surface area and micropore area, total pore volume and micropore volume were calculated. Acidity of the samples was measured by step wise temperature-programmed desorption (STPD) of ammonia using Micromeritics pulse Chemisorb 2700. The procedure for acidity measurement is described in detail in our earlier publication [20]. All the samples were saturated with ammonia at 353 K and later the adsorbed base i.e., ammonia was desorbed by increasing the temperature of the samples in regular intervals. The acidity values measured by desorption of ammonia in the temperature

regions 353–423, 423–573 and 573–723 K are taken to represent weak, medium and strong acid sites, respectively.

2.4. Toluene benzylation

Liquid phase toluene benzylation was carried out over Ca. 0.5 g of the pillared samples. Prior to the experiment, the samples were oven-dried at 373 K for 12 h. The reaction mixture containing 10 cm³ toluene and 1 cm³ benzyl alcohol (94/9.64 mmol) was stirred for 5 h at 353 K and 1 bar. At the end of the reaction, the resultant mixture was analyzed using a GC unit Shemadzu 17 AAFW, with a column of OV-17 (25 m). *Ortho* and *para* isomers of methyl diphenyl methane were identified by GC analysis and were also confirmed by GC-Mass spectroscopy.

2.5. Aniline ethylation

Vapor phase aniline ethylation was carried out on Ca. 0.5 g of clay samples at 673 K, for 4 h, using a feed of aniline:ethanol mixture (1:10 mole) at a feed rate of 12 cm³ h⁻¹ g⁻¹ catalyst. The products collected at 1 h interval for 4 h were analyzed on a Chemito 3865 gas chromatography (GC) unit over a column of Apiezon-L treated with 2% KOH on Chromosorb AW (80/100). *N*-ethylaniline (NEA), *N,N'*-diethylaniline (NN'DEA) and toluidines (others) were the products identified.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of the pristine Na montmorillonite and the modified clays are given in Fig. 1. As can be seen from the shift of the characteristic peak corresponding to $d(001)$ spacing and the intensity of the peak, it is evident that some pillaring has taken place. The d spacing and intensity of the peaks up to $\theta = 10^\circ$ of the samples are given in Table 1. The $d(001)$ spacing of the pristine clay samples increased from 12.62 to 16.72 and 17.38 Å in AIPC (2) and AIPC (Ce, 2), respectively. In the case of Ce-Mont, which is an ion-exchanged sample (not pillared), in-

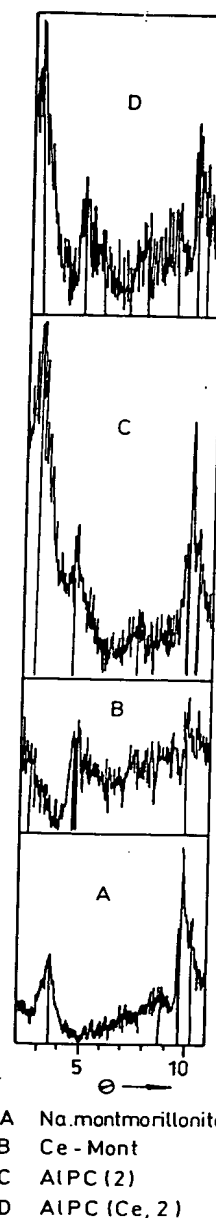


Fig. 1. XRD patterns of montmorillonite and modified montmorillonites A — Na montmorillonite (Source Clays, SWy-1), B — Ce-Mont, C — AIPC(2), D — AIPC(Ce, 2).

Table 1
XRD data of Na montmorillonite and modified montmorillonites

θ (degrees)	Distance (Å)	% Intensity
A — Na montmorillonite (Source Clays, SWy-2)		
3.50	12.62	28.40
8.82	5.02	16.89
9.78	4.53	54.26
10.28	4.32	37.67
B — Ce-Mont		
2.36	18.70	35.34
4.50	9.82	39.22
4.70	9.40	43.69
9.90	4.48	48.16
C — AIPC(2)		
2.64	16.72	84.76
4.54	9.73	34.94
7.60	5.82	19.33
9.98	4.44	59.48
D — AIPC(Ce,2)		
2.54	17.38	73.19
4.62	9.56	53.31
5.46	8.09	37.35
7.46	5.93	37.05
8.96	4.94	42.47
9.92	4.47	59.04

terlamellar spacing increased up to 18.70 Å. However, the characteristic peak is observed to be of low intensity indicating comparatively low $d(001)$ order in the sample.

3.2. Adsorption studies

The nitrogen adsorption–desorption isotherms on the samples are given in Fig. 2. The isotherm on montmorillonite clay is of type IV according to the classification of Brunauer et al. [21]. The adsorption isotherm on the pillared samples is of type I. This type of isotherm is characteristic of microporous materials in which multilayer adsorption of N_2 is sterically hindered. The isotherm of Ce-Mont appears to be intermediate between type I and type IV. So also the isotherm of AIPC(Ce,2), though it resembles more of type I. The hysteresis loop for all the samples is of type B in the classification of de Boer [22], a feature of materials which possess a pore structure built up of parallel plates. Adsorption isotherms on samples Ce-Mont, AIPC(2) and AIPC(Ce,2) according to the BET equation and the Langmuir equation, are given in

Fig. 3. The BET equation considers multilayer adsorption of N_2 ; the Langmuir equation is obeyed by those microporous material in which the multilayer adsorption of N_2 is sterically hindered. Usually porous materials which give type I isotherm obey the Langmuir equation [23]. Zhu and Vansant [24] have discussed the discrepancies in the calculation of surface area of the pillared clays with the Langmuir equation and with the BET equation. They suggest that the actual surface area lies in between BET and Langmuir values. In the case of AIPC(2), the isotherm followed the Langmuir equation, suggesting microporosity, while Ce-Mont obeyed the BET equation, indicating the presence of larger pores. The isotherm of AIPC(Ce,2) seem to obey both the equations. Surface areas as calculated by following BET and Langmuir equations are given in Table 2. The surface area of Na montmorillonite increased from 27.43 to 169.56 $m^2 g^{-1}$ on alumina pillaring (AIPC(2)) and to 184.12 $m^2 g^{-1}$ on alumina pillaring of Ce-exchanged sample (AIPC(Ce,2)). Increase in surface area on pillaring is expected, since the process creates regular porosity. Surprisingly, Ce exchange also enhanced the surface area to 98.60 $m^2 g^{-1}$. However, the increase in surface area on Ce exchange is not as high as in the case of pillared samples. Apparently the ion exchange and subsequent calcination changed the stacking pattern of the pristine clay. The process might have resulted in a layer arrangement similar to the house of cards structure.

The total pore volume of the samples is measured by condensation of N_2 adsorbate at P/P_0 0.95 in the pores of diameter <400 Å by the single point method (Table 2). On pillaring, the total pore volume increased from 0.0348 $cm^3 g^{-1}$ in the pristine clay to 0.1282 $cm^3 g^{-1}$ in case of AIPC(Ce,2). Ce-Mont, despite a low $d(001)$ order like the pristine sample, gave a considerable total pore volume of 0.1052 $cm^3 g^{-1}$.

The linear branch of the isotherm above $P/P_0 = 0.5$ is used for the measurement of the external surface area (A_{ext}) and the micropore volume (V_{mi}) [24]. The parameters are derived using the t -plot of DeBoer [25] or the α_s plot of Sing [26]. The mesopores in clays are mainly the interparticle voids [24] and in pillared clays, mesopores mainly contribute to the A_{ext} . In the present study, the external surface area (A_{ext}) of the samples is calculated from the t -plot and results are given in Table 2. In the case of Ce-Mont, A_{ext} is observed to be almost the same as BET surface area

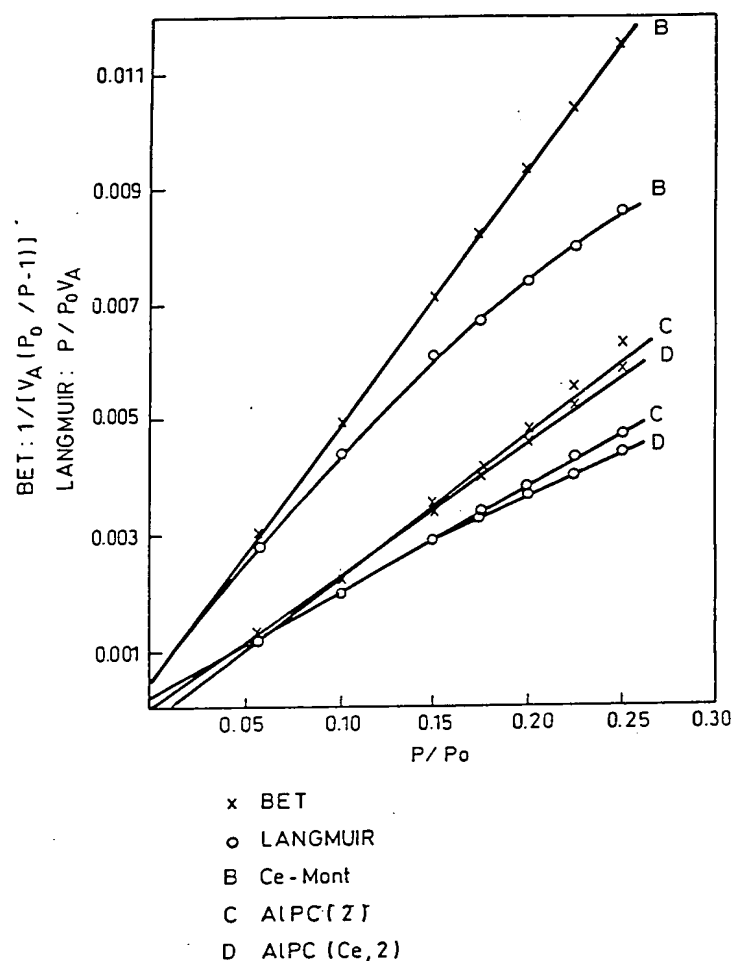


Fig. 3. BET and Langmuir isotherms on modified montmorillonites B — Ce-Mont, C — AlPC(2), D — AlPC(Ce,2).

while calculating the pore diameter. The micropore volume and the pore diameter of AlPC(2) and AlPC(Ce,2) are almost the same. The two pillared samples have different A_{ext} . The higher A_{ext} in

AlPC(Ce,2) compared to AlPC(2) suggests more mesoporosity in the sample. The micropore widths obtained from the adsorption data are comparable with the free spacings (interlamellar distance — thick-

Table 3
Microporosity and mesoporosity of the alumina pillared montmorillonites

Sample code	Catalyst	External surface area, (A_{ext}), $\text{m}^2 \text{g}^{-1}$	Micropore volume (V_{mi}), $\text{cm}^3 \text{g}^{-1}$	Micropore diameter (d_{mi}) ^a , Å	Free spacing ^b , Å
C	AlPC(2)	38.85	0.0638	9.76	7.12
D	AlPC(Ce,2)	100.23	0.0404	9.63	7.78

^a $2 V_{\text{mi}}/A_{\text{BET}} - A_{\text{EXT}}$.

^b $d(001)$: 9.6 Å.

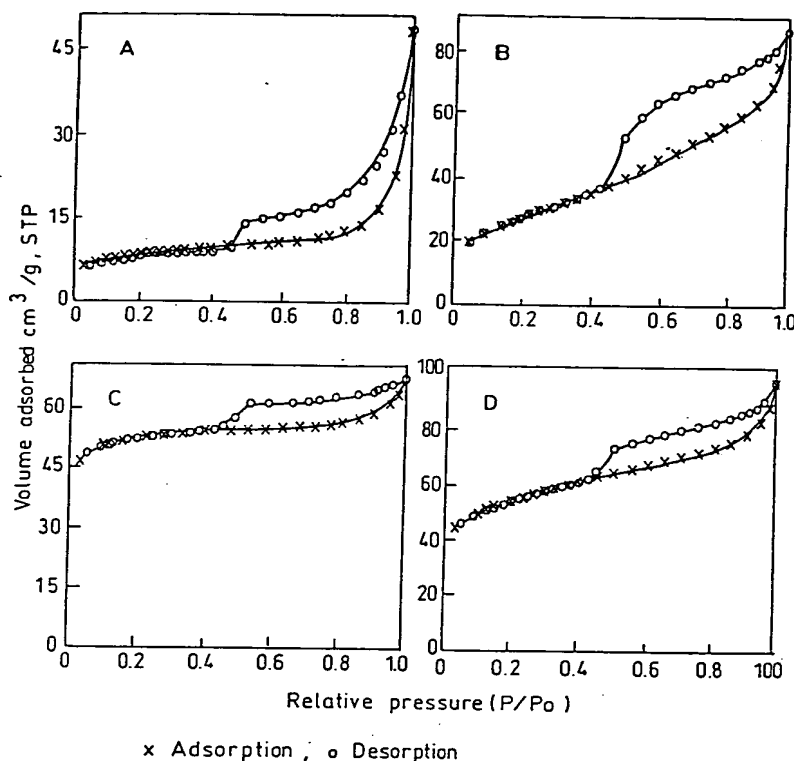


Fig. 2. Nitrogen isotherms A — Na montmorillonite (Source Clays, SWy-1), B — Ce-Mont, C — AIPC(2), D — AIPC(Ce,2).

suggesting that mainly mesopores in the sample contribute to the active sites.

Micropore volumes of the samples are given in Table 3. Pillaring increased the micropore volume from $0.004 \text{ cm}^3 \text{ g}^{-1}$ in Na montmorillonite to $0.064 \text{ cm}^3 \text{ g}^{-1}$ in AIPC(2) and to $0.04 \text{ cm}^3 \text{ g}^{-1}$ in AIPC(Ce,2). Theoretically, the maximum value for

micropore volume in alumina pillared smectites is reported [27] to be nearly $0.12 \text{ cm}^3 \text{ g}^{-1}$. Ce-Mont gave negligible micropore volume.

The pore diameter of micropores in the pillared samples is calculated as mentioned by Zhu and Vansant [24] (Table 3). Micropores in pillared clays have slit shapes. This has been taken into account

Table 2
Physical parameters of Na montmorillonite and modified montmorillonites

Sample code	Catalyst	BET surface area, $\text{m}^2 \text{ g}^{-1}$	Langmuir surface area, $\text{m}^2 \text{ g}^{-1}$	External surface area (A_{ext}) ^a , $\text{m}^2 \text{ g}^{-1}$	Total pore volume ^b , $\text{cm}^3 \text{ g}^{-1}$	Average pore diameter ^c (Å)
A	Na-Mont (Source Clays)	27.43	39.63	18.81	0.0348	50.7760
B	Ce-Mont	98.60	146.65	101.34	0.1052	42.6818
C	AIPC(2)	169.56	237.18	38.85	0.0949	22.3798
D	AIPC(Ce,2)	184.12	262.51	100.23	0.1282	27.8550

^a Calculated from the t -plot.

^b N_2 condensation at $P/P_0 = 0.95$ in the pores of diameter $< 400 \text{ Å}$.

^c $4V/A$ by BET.

ness of clay layer (9.6 \AA) obtained from the XRD measurements (Table 3). The slight variations in the values may be a contribution from the amorphous nature of part of the sample or the unpillared portion or due to a difference in the pillar density of the layers. The isotherms, total pore volume, A_{ext} , V_{mi} and pore diameter of AIPC(Ce,2) suggest presence of both micropores and mesopores in the sample. Probably, house of cards structure of Ce-Mont is partially retained in AIPC(Ce,2) (Fig. 4).

AIPC(2) and AIPC(Ce,2) were calcined at different temperatures (673, 773, 873 and 1073 K) and the surface area of the samples was measured. AIPC(2) and AIPC(Ce,2), calcined at 673 K gave a BET surface area of 169 and $184 \text{ m}^2 \text{ g}^{-1}$, respectively. The surface area of the samples was found to be almost the same on calcination upto 873 K. On further calcination to 1073 K, there was a remarkable reduction of 71% in AIPC(2) and 65% in AIPC(Ce,2) in the surface areas of both the samples, implying that the prepared samples are thermally stable upto 873 K.

Al^{3+} proxying for Si^{4+} in the tetrahedral coordination gives rise to a net negative charge on aluminosilicate. A charge balancing H_3O^+ associated with such tetrahedral Al^{3+} corresponds to a Brønsted acid site. Al^{3+} in a three-fold coordination occurring at an edge, or arising from a Si–O–Al bond rupture or by dehydroxylation of a Brønsted site, functions as a Lewis acid site [28]. Pillaring increases the acidity of the clay. By propping up the clay layers, the process exposes the Brønsted and Lewis acid sites of the layers. Furthermore, the pillars add acid sites to the already existing hydroxyl groups and to Al. Alumina pillars are known to increase especially the Lewis acidity [16]. Among the alumina pillared samples prepared with different OH/Al ratios, the variation of acidity in the weak and medium range is not conspicuous (Fig. 5); the acidity as measured by desorption of NH_3 in the temperature region 573–723 K, increased with OH/Al ratio and reached a maximum for the sample with OH/Al = 1.5. The total acidity and its distribution in the three temperature regions for AIPC with OH/Al = 1.5, 2 and 2.25 is almost the same. Comparison of STPD of ammonia of Ce-Mont, AIPC(2), AIPC(Ce,2) (Fig. 6) shows that the pillared samples have much stronger acidity than Ce-Mont. The total acidity of the two pillared samples is almost

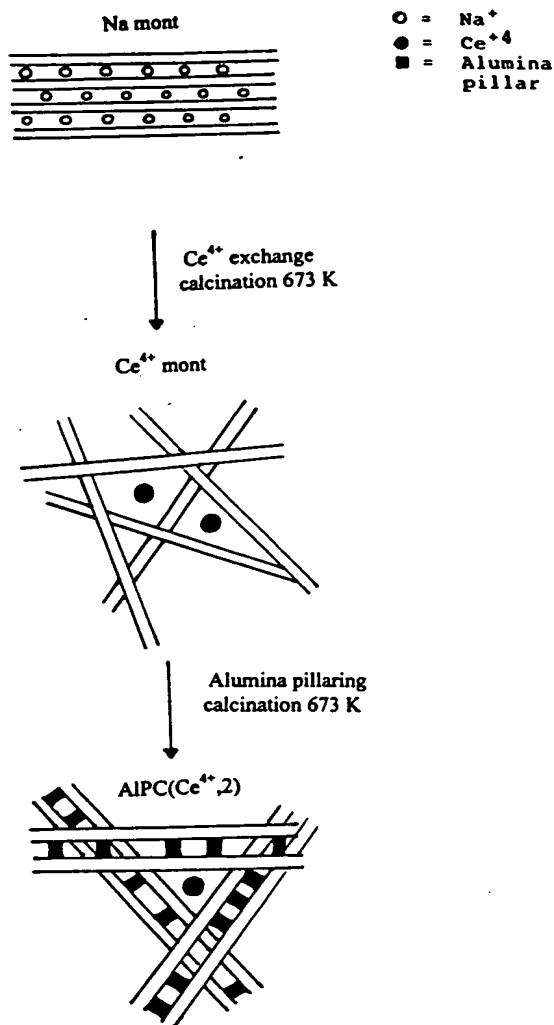


Fig. 4. Schematic representation of delaminated structure of Ce-Mont and partially delaminated structure of AIPC(Ce,2).

the same ($75.6 \times 10^{-2} \text{ mmol g}^{-1}$ — AIPC(2) and $69.8 \times 10^{-1} \text{ mmol g}^{-1}$ — AIPC(Ce,2)) but the distribution of acidity in three temperature ranges is different. In case of AIPC(2), the weak and medium acidity are almost equal, but the strong acidity represented by the ammonia desorption in the temperature range 573–723 K is comparatively more. On the other hand, in the case of AIPC(Ce,2) the acidity is almost equally distributed in the three regions. Almost equal

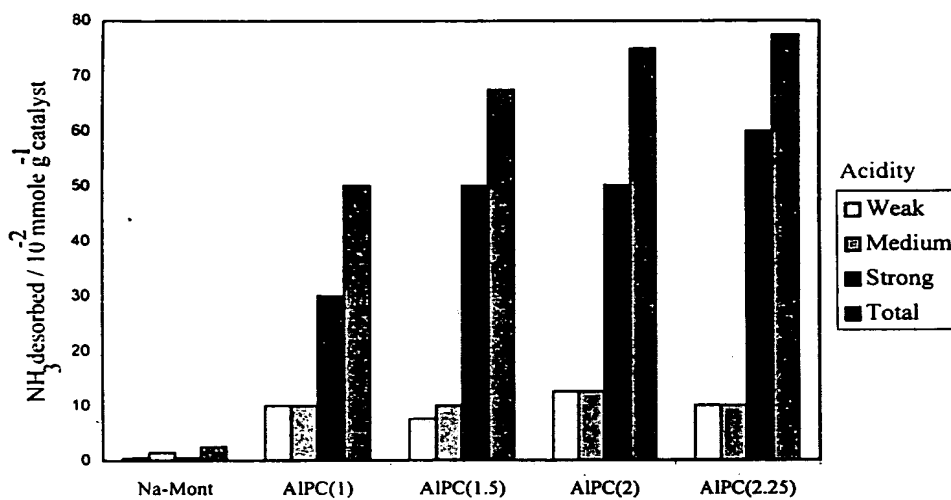


Fig. 5. STPD of ammonia over Na montmorillonite and alumina pillared montmorillonites.

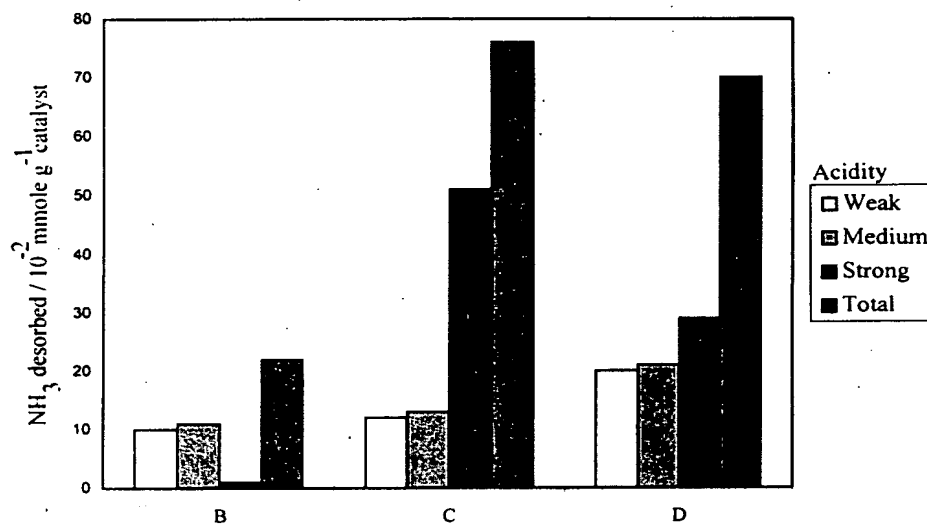


Fig. 6. STPD of ammonia over modified montmorillonites B — Ce-Mont, C — AIPC(2), D — AIPC(Ce,2).

total acidity of the samples AIPC(2) and AIPC(Ce,2) but different distribution of acidity in the three temperature regions suggests that, though Ce ions do not contribute to the acidity, they lead to a structurally dissimilar alumina pillared clays with different acid site distribution.

4. Catalytic activity

4.1. Toluene benzylation

Toluene benzylation is one of the well studied reactions. Over the mesoporous catalysts like ion-

Table 4

Toluene benzylation carried out at 353 K for 5 h.

Clay sample	% Conversion of benzyl alcohol	% Selectivity		
		<i>o</i> -methyl diphenyl methane	<i>p</i> -methyl diphenyl methane	Benzyl ether
Montmorillonite K10	100	56	44	—
Ce-Mont	100	49	51	—
AIPC(1)	100	56	44	—
AIPC(1.5)	98	39	42	19
AIPC(2)	55	35	39	26
AIPC(2.25)	51	47	38	15
AIPC(Ce,2)	100	36	64	—

exchanged montmorillonite K10, 100% conversion is reported with nearly 1:1 isomeric distribution of *ortho* and *para* methyl diphenyl methane [29]. On HZSM-5, Coq et al. [30] have reported a low conversion (40%) and related it to the narrow pore size of the zeolite.

On alumina pillared clays, it is observed that there is a gradual decrease in conversion of benzyl alcohol (Table 4) with the increase in OH/Al ratio from 1 to 2.25. As the ratio increases, the number of polymeric cations in the pillaring solution increase resulting in a higher extent of pillaring and development of microporosity in otherwise lamellar structure. The partly pillared samples AIPC(1 and 1.5) have considerable unpillared spaces along with the micropores. These spaces allow easy diffusion of the reactant molecules and result in 100% conversion of benzyl alcohol to give *ortho* and *para* methyl di phenyl methane. Coq et al. [30] have carried out the benzylation reaction using toluene and benzyl chloride over HZSM-5, H-Beta and HY catalysts. They have reported large differences in the activity of the catalysts for the reaction. The most active sample was found to be the one which possessed large volume in mesopores i.e., HY20. Very low activity exhibited by HZSM-5 has been related to narrow pore size of the zeolite and absence of the mesoporous volume. A_{ext} , V_{mi} and total pore volume of AIPC(2) suggest predominantly microporous structure. This may be a reason for the low conversion (55%) on the sample. The micropores may be restricting the diffusion of reactant and product molecules analogous to the situation in HZSM-5 as reported by Coq et al. [30].

Benzyl ether is formed as a side product on AIPC(1.5, 2 and 2.25) by the condensation of benzyl

alcohol. Yadav et al. [31] also have reported formation of benzyl ether and alkylated benzyl ethers as major side products in benzylation of toluene. The formation of benzyl ethers were noticed on those alumina pillared montmorillonites which have more acid sites that desorb ammonia in the temperature range 573–723 K.

AIPC(Ce,2) gave nearly 100% conversion for toluene benzylation, similar to montmorillonite K10; but the selectivity pattern of the two catalysts is different. Low selectivity of 36% to the *ortho* arylated product on AIPC(Ce,2) (montmorillonite K10 — 56%) may be due to the presence of smaller pores in the pillared sample compared to the mesoporous montmorillonite K10.

4.2. Aniline ethylation

Na montmorillonite is found to be inactive for aniline ethylation (Table 5). Over the alumina pillared montmorillonites, with the increase in OH/Al ratio

Table 5

Aniline ethylation carried out at 673 K, feed rate $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ and 1 bar

Clay sample	% Conversion of aniline	% Selectivity		
		NEA	NNDEA	Others
Na -Mont (Source Clays)	—	—	—	—
Ce-Mont	55	52	40	7
AIPC(1)	76	47	29	24
AIPC(1.5)	61	50	26	24
AIPC(2)	51	65	28	7
AIPC(2.25)	50	63	27	10
AIPC(Ce,2)	81	51	30	19

from 1 to 2.25, the aniline conversion decreased from 76% to 50%. Aniline alkylation has been studied [32–34] over modified silica and montmorillonite K10. It was observed that, though the presence of a certain amount of acidity especially in weak and medium range are essential for the reaction, surplus acidity does not affect the conversion. Different alumina pillared samples, despite possessing considerable surface area and almost same weak and medium acidity showed decreasing aniline conversion. Among all the alumina pillared samples, aniline conversion was the lowest (51%) over AIPC(2). These results once again suggest the restricted diffusion of the reactant and product molecules through the micropores. Low aniline conversion (55%) over Ce-Mont may be due to its comparatively low surface area ($98.60 \text{ m}^2 \text{ g}^{-1}$) and total acidity ($21.65 \times 10^{-2} \text{ mmoles g}^{-1}$). However, the corresponding alumina pillared form i.e. AIPC(Ce,2) gave aniline conversion of 81% (surface area — $184 \text{ m}^2 \text{ g}^{-1}$ and total acidity — $69.79 \times 10^{-2} \text{ mmoles g}^{-1}$). The results of vapor phase aniline alkylation reaction suggest that the effect of porosity of the pillared clays is observed on the conversion of aniline, but not on the selectivity pattern of the alkyl anilines.

5. Conclusions

Na montmorillonite (SWy-2) was ion-exchanged with Ce ions and pillared with poly hydroxy aluminium ions. XRD results of the samples supported that pillaring has taken place, as evidenced from the $d(001)$ spacing and the intensity of the peaks. Though the interlamellar space widened in the Ce-exchanged sample (Ce-Mont), the characteristic peak at $\theta = 2.36^\circ$ showed low intensity, indicating a lack of $d(001)$ order as compared to the pillared samples. BET and Langmuir surface area, total pore volume, external surface area (A_{ext}) and micropore volume (V_{mi}) are calculated from N_2 adsorption-desorption data. N_2 isotherm on Na montmorillonite is of type IV which is typical for lamellar solids. Type II isotherms, characteristic of microporous material were observed for the Alumina pillared samples. Ce-exchanged montmorillonite gave an isotherm intermediate between types II and IV. Nearly the same BET and external surface area of Ce-Mont suggest mesoporosity in the

sample. AIPC(2) and AIPC(Ce,2) samples have the same V_{mi} and micropore widths, suggesting nearly the same extent of microporosity within the samples. However, a higher external surface area (A_{ext}) of AIPC(Ce,2) indicates additional mesoporosity in the sample. Probably, house of cards structure of Ce-Mont is partially retained in AIPC(Ce,2). The prepared alumina pillared samples are found to be thermally stable up to 873 K, as evidenced by the maintenance of the surface area. However, calcination beyond 873 K resulted in the reduction of surface area, indicating collapse of structure. Pillaring enhanced the strong acidity of the samples measured by desorption of ammonia in the temperature range 573–723 K. Though the total acidity of the two pillared samples, AIPC(2) and AIPC(Ce,2), was found to be almost the same, the distribution of the weak, medium and strong acidity is different. This may be due to their structural dissimilarity. Ce-Mont and AIPC(Ce,2) gave 100% conversion of benzyl alcohol. Over the same set of catalysts, aniline conversion is observed to be 55% and 81%, respectively. Low aniline and benzyl alcohol conversions (55% and 51%) are observed over AIPC(2) due to restricted diffusion of the reactants through the micropores.

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